

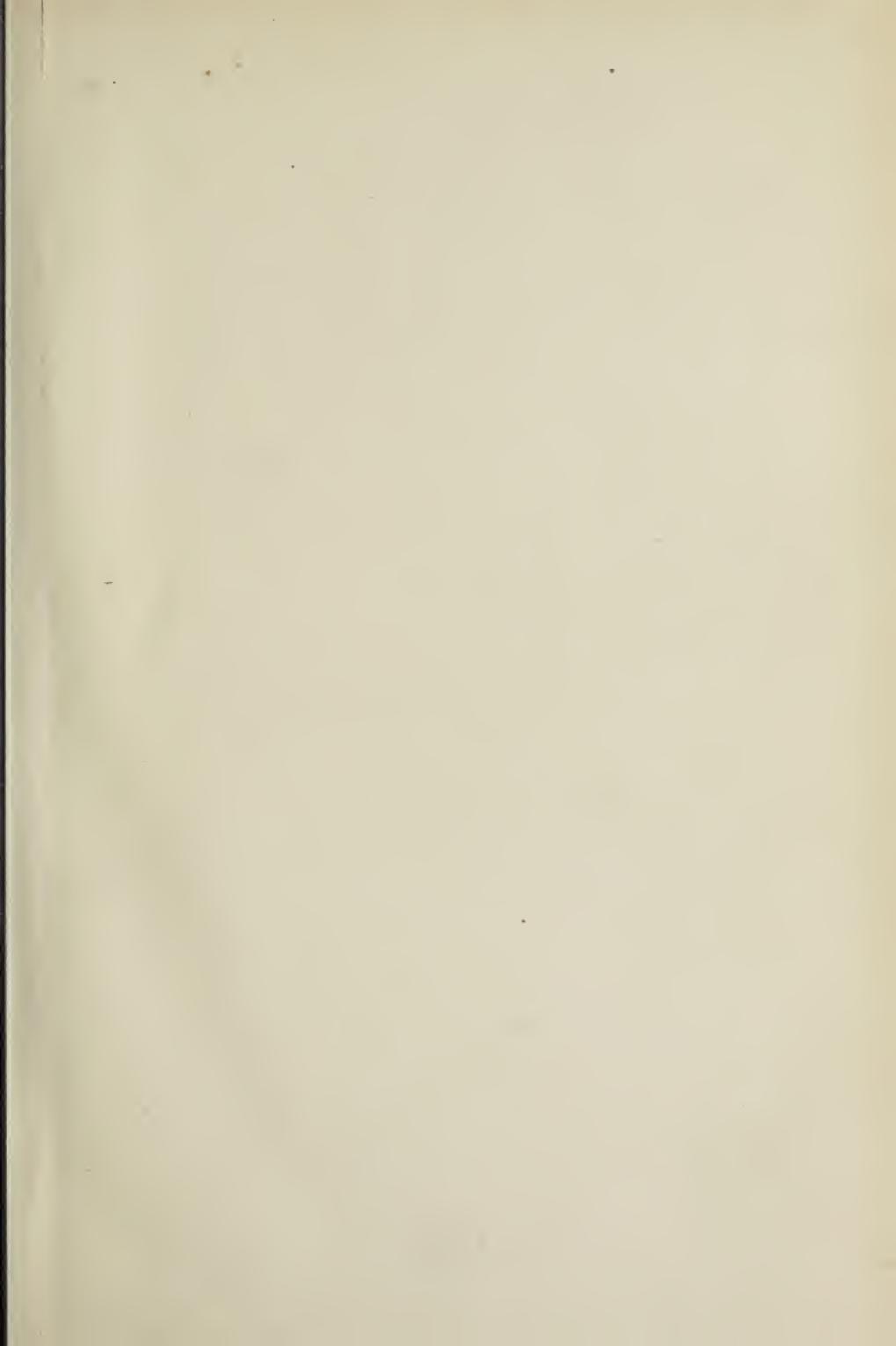


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# PIGMENTS, PAINT

AND

# PAINTING



# PIGMENTS, PAINT AND PAINTING

*A PRACTICAL BOOK FOR PRACTICAL MEN*

BY

GEORGE TERRY



London

E. & F. N. SPON, 125 STRAND

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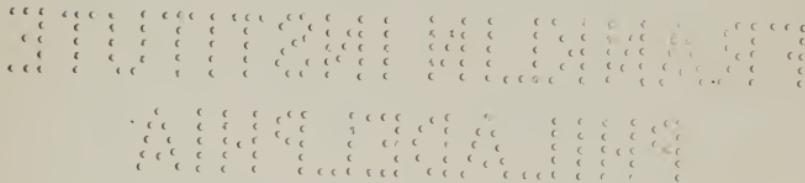
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## INTRODUCTION.

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In days gone by, the painter who served the usual term of apprenticeship was deemed to have done all that was required to qualify him for his trade. He may have learned little or much, but he had "served his time," and that was all that was expected of him. So far as it went, the training was good, because it was nothing if not practical, and practice is an essential element of skill. But nowadays such a training can only be considered partial; mere practice, without any scientific knowledge of the principles which underlie it, is but half a qualification for the workman who aims at being really a master of his trade.

When competition was unknown, and the low prices of raw material offered no inducement for passing off inferior or fraudulent substitutes, there was less need for a high degree of knowledge. But under modern conditions, the painter who is unable to gauge the qualities of the materials he uses, and who is ignorant of the rules which govern those qualities, and of the principles which determine the use of this and the rejection of that article, cannot long survive in the struggle for supremacy or even livelihood.

Hence the need for a handbook such as this volume aims at being. Granted that our technical schools and colleges are affording a liberal and invaluable education to the work-

man who will avail himself of the opportunities given him, still a man does not remain for ever at school, and he needs a guide-book, handy of reference and accessible in price, to refresh his memory and supplement the information gained in the class-room and workshop.

To fulfil this useful purpose is the aim and object of this unpretending volume.

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# P A I N T.

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## CHAPTER I.

### P R E L I M I N A R Y.

**Colour.**—The term “colour” is inappropriately given by common usage to material substances which convey a sense of colour to the human eye, but is properly restricted to that sense itself. The material colour should be called “pigment” or “dyestuff” in the raw state, and paint when compounded with other substances for application in the form of a coating.

The sense of colour is due to light. In the absence of light there is no colour, only blackness; and black is really no colour, but an absence of colour. Very many conditions combine to cause different colour sensations, some of which are understood, while others we are not able to explain.

For instance, take the action of heat upon a solution of chloride of cobalt. As soon as the liquid becomes warm, the pink colour disappears and gives place to blue; but on pouring water into it, the blue vanishes and the pink reappears. Again, on heating the blue crystals of sulphate of copper they become white, but the blue colour comes back when water is added, and the solution assumes a deeper tint as it dissolves more of the white powder.

If all the rays are cut off from an electric light except those which are in and beyond the violet, and a flask con-

taining a solution of sulphate of quinine is held in that portion of the spectrum, it will become luminous. The same thing will occur even more strikingly on placing a piece of uranium glass in the ultra-violet rays. The explanation of this phenomenon is that beyond those rays which give light there are others which do not give light, i.e. which do not cause us to experience the sensation of light; the reason being that their vibrations are too rapid. But when certain other substances, such as sulphate of quinine, or a thin slip of uranium glass, are placed in the path of the rays, this rapid motion is arrested and modified, and these rays, which in themselves are not luminous, are reflected back to our eyes as luminous rays. The rapidity of the vibrations being moderated, our retinas become sensible to them as rays of blue light.

Colour does not depend only upon chemical composition nor solely upon the aggregation of the particles, but upon these and other things besides not yet explained. All matter is in a state of motion. If you heat a substance you communicate an increased activity of motion to the particles of which it consists. When certain coloured rays of light are falling upon a substance, these coloured rays of light have a motion peculiar to themselves. It may be that the degree of motion in that substance, either existing in it naturally without heating, or communicated to it by artificial heating, is such that these rays of light are precisely those which that substance is not capable of sending back to our eyes. They are then absorbed or destroyed in some way, by the particular state of that substance upon which they fall; and those rays which the substance is capable of reflecting back are mainly sent back to our eyes. Certain colours, such as blue, yellow, and green, absorb certain rays more or less perfectly, and reflect back in the main blue, yellow, and green to our eyes. Hence it is incumbent on those who are studying colour, and who are interested in the purity and permanency of colour, to comprehend at least

the principles of that science of light which tells of the action of light upon various bodies that are used as pigments in painting.

If we put together two substances one of which destroys or modifies the chemical condition or state of the other, then certainly one of those substances, and very probably both, will lose the colour which it had before it came into contact with the other. It is therefore most important that all engaged in the preparation and use of colours should make a study of this science of light. Of almost equal value is a study of the science of heat. We have seen what heat can do in changing the conditions of a substance. To give another instance. The black sulphide of mercury, after sublimation by heat, exhibits properties, imparted to it by the heat, which it did not possess before, i.e. it can, by trituration, be brought to display a red colour.

On showing the spectrum on a screen, if some solution of soda or other sodium salt be held in the course of the light, almost all the coloured rays but one will be cut off, and a little band is seen in the yellow part of the spectrum. This is because the sodium flame is almost "monochromatic," or single-lined: it cuts off all the colours but the yellow. Again, if metallic thallium is held in the flame, the only band remaining in the spectrum will be the green; and if a lithium salt, the only surviving colour will be red.

**Pigments.**—The term "pigments" is applied to those colouring matters which are mixed in a powdery form with oil or other vehicle for the purpose of painting. They differ in this respect from the dyestuffs, which are always employed in solution. A very large proportion of the pigments in common use are derived from the mineral kingdom, the most notable exceptions being found in the blacks and lakes. All pigments are required to possess "body," or density and opacity; to be insoluble in water and most other solvents, except the stronger mineral acids; and to be inert, or incapable of exercising chemical or other influence

on each other or on the vehicle or drier with which they are mixed prior to use. They may be conveniently classified according to their colours in the first place, reserving the consideration of their preparation for use for a later chapter. The chief classes are Blacks, Blues, Browns, Greens, Reds, Whites, and Yellows.

## CHAPTER II.

### BLACKS.

ALL the black pigments in use owe their colour to carbon, and all are produced by artificial means, no natural form of carbon possessing the requisite qualities.

Several manufactured carbonaceous substances are known in commerce under the generic name of "Blacks." The most important of these are animal-black, bone-black, Frankfort-black, ivory-black, and lamp-black. They are usually obtained by carbonising organic matter, particularly bones, in closed vessels or crucibles, or by collecting the soot formed by the combustion of oily, resinous, and bituminous substances. Other blacks than those enumerated are manufactured, but only on so small a scale as to be of no commercial importance.

Carbon, lamp, and vegetable blacks consist almost entirely of carbon, containing usually from 98 to 99½ per cent. of that substance, the residue consisting of a little ash, water, and occasionally unburnt oil. Bone and ivory blacks, on the other hand, are chiefly composed of mineral matter, which may amount to 65 or 75 per cent. and is mainly represented by phosphate of lime. Their actual colouring matter, the carbon, only constitutes 15 to 30 per cent. of the mass. The balance is water and unburnt animal tissue. Blacks prepared from animal matters other than bone and ivory carry 40 to 80 per cent. of carbon, and their mineral matter is generally in the form of carbonates of lime and of the alkalies.

The principal impurity to be watchful of in the vegetable and lamp blacks is a small quantity of oily matter which

may seriously interfere with their drying qualities. They should leave very little ash after being burned in a crucible. Bone and ivory blacks are sometimes valued as much for their mineral matter as for their colouring matter. The proportion of this mineral matter is ascertained by heating a certain weight of the black to red heat in a crucible till every trace of black has disappeared, and then weighing the residue. The residue should next be boiled in strong hydrochloric acid till it is dissolved; if there is any which will not dissolve it is most probably barytes, which has been added as an adulterant and to make the black weigh heavy. When the solution is complete, the addition of ammonia will throw down a precipitate of phosphate of lime, which should equal 60 to 70 per cent. of the original weight of mineral matter. If much less than this, it is likely that whiting or gypsum has been mixed with the pigment. As carbon is not acted upon by acids or alkalies, it follows that all pure carbon blacks are in themselves perfectly stable and permanent pigments, and that they exert no influence on other pigments with which they may be mixed.

**Animal-black.**—This substance is almost identical with bone-black, but is generally in a more finely divided state. Any animal refuse matter may be used in its preparation, such as albumen, gelatine, horn shavings, &c. These are subjected to dry distillation in an earthenware retort. An inflammable gas is given off, together with much oily matter, ammonia, and water, while a black carbonaceous mass is left behind. This is washed with water and powdered in a mill, the product being animal-black. It is largely used in the manufacture of paint, printing ink, and blacking.

**Bone-black.**—When bones are heated in a retort or crucible, the organic constituents are decomposed and carbonised. A mixture of combustible gases is given off; some of these do not condense on cooling, others condense in the form of a heavy oil, called bone-oil. Also much water containing tarry water and ammoniacal salts in solution passes

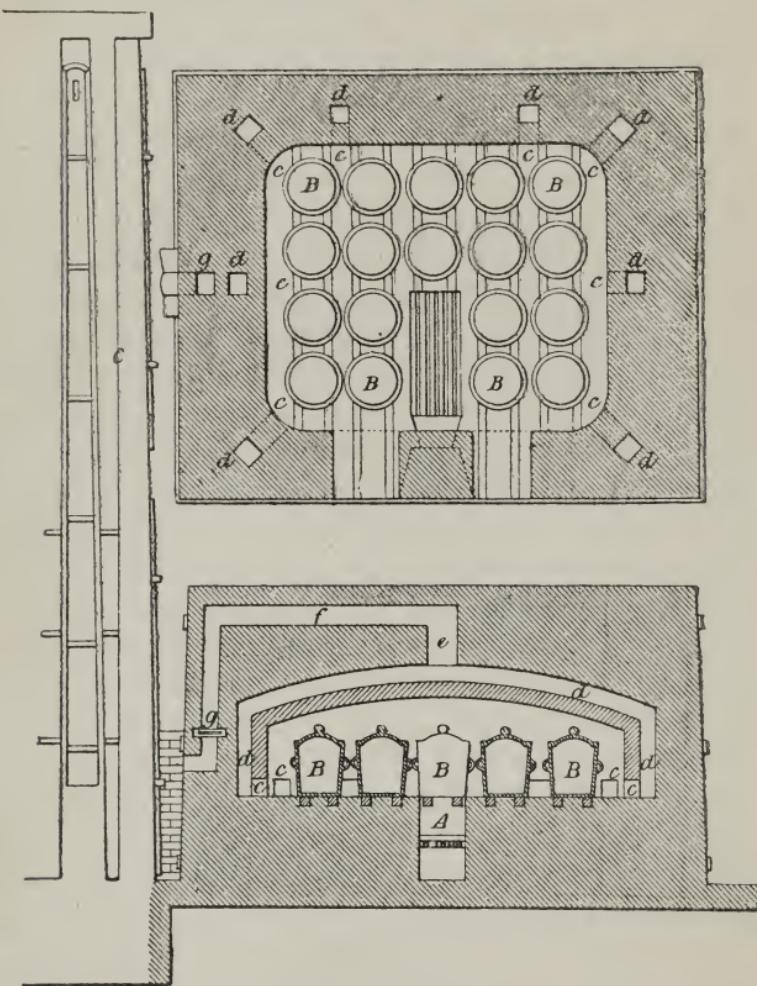
ever. The residue in the retort or crucible consists of finely divided carbon, in intimate mixture with the inorganic constituents of the bones: this mixture constitutes ordinary bone-black, or animal charcoal, as it is sometimes called. The inorganic portion may, if required, be removed by washing the residue in dilute hydrochloric acid.

The process, as worked on the large scale, is carried on in different ways, according as it is desired to collect the volatile condensable portion of the distillate, or to allow it to escape. In the latter case, when it is required to obtain only bone-black, the apparatus employed is of a very simple nature, and the amount of fuel needed is comparatively small. The carbonisation is effected in fire-clay crucibles, 16 in. high and 12 in. diameter. These are to be preferred to crucibles made of iron, which were much used at one time, since they do not lose their round form when subjected to a high temperature; in consequence of this, they fit more closely together in the furnace, less air can penetrate, and therefore less of the charcoal is consumed by oxidation. The furnace is an ordinary flat hearth, having a superficial area of about 40 square yards, and is covered in with a flat arch, all of brickwork. The fireplace is situate in the middle of the hearth; the crucibles are introduced through doors in the front, which are bricked up when the furnace is filled; each furnace holds eighteen crucibles. The crucibles, filled with the coarsely broken bones, are covered with a lid luted on with clay. To economise fuel, the furnaces should be in a row, and placed back to back.

The arrangement of the furnace and pots is shown in Figs. 1 and 2. A is the fireplace; B, the crucibles, eighteen in number, spread over the floor of the furnace in a single layer; c, d, e, and f are the flues for conducting away the heated gases arising from the calcination of the bones, as well as the waste heat itself; the last portion of the flue is fitted with a damper g. The furnaces are intended to be built in fours, back to back, the waste heat serving in a great measure to

conduct the operation of the revivifying apparatus placed in the centre of the group, and marked C.

When the furnace is filled and the doors are bricked up, the



Figs. 1 and 2.—BONE-BLACK FURNACE.

heat is slowly raised to redness, at which point it is kept for six or eight hours. The combustible gases are evolved and consumed in the furnace as the bones begin to decompose, and by this means so much heat is produced that only a

small quantity of fuel is needed to maintain the required temperature. When the carbonisation is complete, the doors are taken down and the crucibles are removed to cool, their places being immediately filled with fresh ones. The heat must be kept as uniform as possible throughout the process : if it be not sufficiently high, the bone-black will contain a portion of undecomposed organic matter, which renders it quite unfit for use ; if, on the other hand, the temperature be raised too high, the bone-black will become dense and compact, whereby its efficacy as a decoloriser is much reduced. When the charcoal in the crucible has become perfectly cool, it is removed and crushed. When required for decolorising or deodorising purposes, it is only roughly broken up into small lumps, in which form it is most readily applicable. The crushing is effected by means of two grooved cylinders, consisting of toothed discs, alternately 10 and 12 in. in diameter. These are so placed that the 10-in. discs of one cylinder are opposite the 12-in. discs of the other, and thus, in revolving, the carbonised bones are crushed to fragments between them, but are not reduced to powder. They are passed successively through six of these mills, the cylinders of each couple being nearer to each other than the last. Finally the crushed bones are carefully sieved ; the powder is placed apart from the lumps, again passed through finer sieves, and sorted out into different sizes.

A furnace such as that described above will carbonise four charges of bones in one day, each charge being more than half a ton in weight. With careful work, the bones will yield 60 per cent. of bone-black, or more than one ton daily.

If it be required to condense the volatile gaseous products of the carbonisation, this process is conducted in retorts similar to those used in the manufacture of acetic acid from wood : these are so arranged that the whole of the gaseous products are condensed and collected. The aqueous portion of the distillate is usually evaporated down to obtain salts of

ammonia; the uncondensable gases may be employed for illuminating purposes. The manufacture of bone-black is usually carried on in the neighbourhood of large towns, where a good supply of bones may be readily obtained.

Ordinary bone-black has about the following composition: Phosphate and carbonate of lime, and sulphide or oxide of iron, 88 parts; charcoal, containing a small quantity of nitrogenous matter, 10 parts; silicated carbide of iron, 2 parts. The decolorising properties of bone-black are due solely to the presence of the charcoal.

When intended for use as a deodoriser or decoloriser, bone-black should be kept carefully excluded from the air, for by exposure it loses this power to a great extent, and becomes almost inert. That which has been freshly burned is therefore best for these purposes.

The cost of production of bone-black may be calculated as follows:—

	£ s. d.		£ s. d.
4 tons fat bones at 4s. per cwt. .. .. ..	16 0 0	Rent and taxes .. ..	0 8 0
27½ bushels coals .. .. ..	1 3 9	Interest, repairs, and wear and tear .. ..	0 7 2
2 firemen .. .. ..	0 4 9	Contingencies and trans-	
4 workmen .. .. ..	0 8 0	ports .. .. .. ..	0 2 4
1 carman.. .. .. ..	0 2 4		
2 horses .. .. .. ..	0 5 7		<hr/> £20 7 3
Breaking up the bones..	1 5 4		

Produce:—

Black, 60 per cent., say 38 cwt. in grains, at

14s. 3d. .. .. .. .. .. ..	13 10 9
10 cwt. fine, at 5s. 6d. .. ..	1 7 8

Fat, 6 per cent., say 5 cwt. at 31s. 8d. .. ..	7 18 4
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	<hr/> £22 16 9	22 16 9
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Profit .. .. .. .. ..	<hr/> £2 9 6
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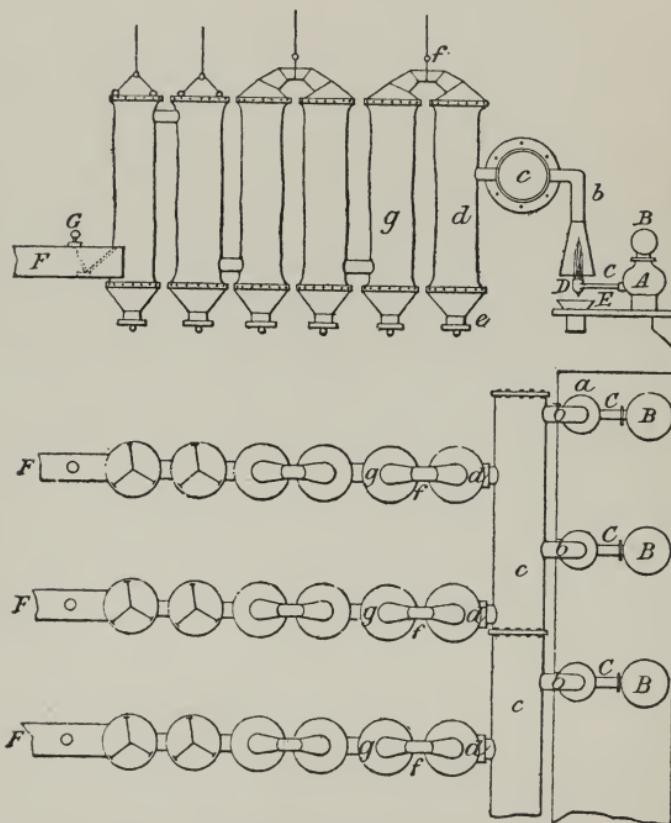
Bone-black never has the depth or brilliancy of lamp-black, but it mixes well with either water or oil, and though a slow drier as an oil paint, is permanent and not high priced.

**Frankfort-black or Drop-black.**—This is a black powder obtained from dried vine-twigs carbonised to a full black and then ground very fine. On a large scale it is prepared from a mixture of vine-twigs, wine-lees, peach-stones, bone-shavings, and ivory refuse. It varies in shade according as the animal or vegetable charcoal is in excess; when the latter predominates, the powder is of a bluish colour; but when there is an excess of animal charcoal, it has a brownish tinge. It is customary to wash the powder well when first made, in order to remove any soluble inorganic impurities. The finest Frankfort-black is probably the soot obtained from the combustion of the materials mentioned above. It makes an excellent pigment, and is extensively used by copperplate engravers in the preparation of their ink. Drop-black is simply Frankfort-black ground exceedingly fine, mixed with a little glue water, and dried in pear-shaped drops for sale.

**Ivory-black.**—Ivory-black is a beautiful black pigment prepared by carbonising waste fragments and turnings of ivory. These are exposed to a red heat for some hours in crucibles, great care being taken to avoid overheating or burning. When quite cold, the crucibles are opened, and the contents are pulverised, the richest coloured fragments being kept apart for the best quality. The powder is then levigated on a porphyry slab, washed well with hot water on a filter, and dried in an oven at a temperature not exceeding 212° F. The product is of a very beautiful velvety black colour, superior even to that obtained from peach-kernels, and quite free from the reddish tinge which so often characterises bone-black. Ivory-black, like Frankfort-black, is employed by copperplate printers in the preparation of their ink. Mixed with white lead, it affords a rich pearl-grey pigment.

**Lamp-black.**—Lamp-black is an exceedingly light, dull-black powder, formed by the imperfect combustion of oils, fats, resins, &c. It may be prepared on a small scale by

suspending a small tin-plate funnel over the flame of a lamp fed with oil, tallow, or crude naphtha, the wick being so arranged that it shall burn with a large and smoky flame. Dense masses of this light carbonaceous matter gradually collect in the funnel, and may be removed from time to time. The funnel should be furnished with a metal tube to convey



Figs. 3 and 4.—APPARATUS FOR MAKING LAMP-BLACK.

the gases away from the room, but no solder must be used in making the connections.

An especially fine quality of lamp-black is obtained from bone-oil, deprived of the ammonia with which it is always contaminated. It is manufactured on a commercial scale by means of the apparatus shown in Figs. 3 and 4. The oil is

contained in the lamp A and kept at a constant level by means of the globular vessel B, which is also filled with oil and inverted over A. The oil flows from the lamp into the tube C, which is bent upwards at the farther extremity on a level with the oil in the lamp. A cotton wick is supplied to the bent end of the tube, as well as a little spout D, for conducting away any oil that may overflow into the receptacle E placed beneath. A conical hood *a* surrounds the flame of the lamp and terminates in a tube *b*, through which are conveyed the sooty products of the combustion of the oil into the wide lateral tube *c*, arranged to accommodate the smoke from about a dozen such lamps placed at intervals of about 6 feet, as indicated in the figures. The effect of this wide tube *c* is not only to cool the smoke, but also to collect the water and other liquids condensed. The smoke and vapours pass hence into *d*, the first of a series of sacks made of closely woven linen, about 10 or 12 feet long and 3 feet in diameter, closed at the bottom with a trap or slide *e*, and formed at the upper and lower ends of sheet-copper tubing made funnel-shaped. The upper one of these is prolonged into an additional pipe *f*, by means of which the smoke arrives at the second sack *g* in the series, thence finding its way to the third, and so on till the last sack of the row is reached. In connection with the last sack of each row is placed a horizontal flue F, in which are arranged frames covered with wire gauze and mounted on hinges. Their purpose is to retain the small remaining portions of lamp-black passing out with the smoke from the sacks. The meshes of the gauze are constantly getting filled up with soot, which necessitates a periodical checking of the draught for its removal. This is done by means of the rod G, which, when raised and allowed to fall suddenly, jerks the accumulated mass off the gauze. The current of air passing through the entire apparatus can be regulated by a damper placed at the entrance to the chimney in which the flue F embouches. At regular intervals, the mouthpieces in the lower ends of the

sacks are removed, and their contents are shaken out separately and collected according to their various qualities. That gathered from the first sack in each row should always be kept apart from the remainder, as it is much contaminated by the presence of resinous and tarry matters.

The old-fashioned method of preparing lamp-black from the incomplete combustion of gas tar is conducted in an apparatus resembling that shown in Fig. 5. The furnace *a*, lined with fire-brick, contains a kettle *b*, and is surmounted by a large thick cast-iron hood *c*, communicating with a stone or brick condensing chamber, divided by means of perforated partition walls into three unequal sized compartments *d*, *e*, *f*, wherein the black is deposited. A chimney *g* delivers

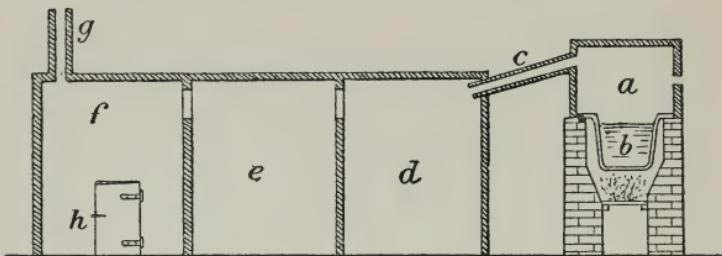


Fig. 5.—APPARATUS FOR MAKING LAMP-BLACK.

uncondensed vapours into the atmosphere. In working, the furnace is first brought to a red heat, then the kettle *b*, charged with tar, is introduced. As a charge is finished, more tar is added, with occasional stirring, till the kettle becomes inconveniently full of residue, when it is withdrawn and a fresh one replaces it. The residue is chipped out and used as fuel. The black is removed weekly through the door *h*. It is of good quality and colour so long as the combustion is conducted with a minimum of air, admission of which is controlled at the furnace. The yield is about 25 per cent. of the weight of the tar; and one furnace should treat a ton of tar in a week. One workman can manage several furnaces.

An improved process has been introduced by Martin and Grafton for the preparation of lamp-black from coal-tar, which affords a very good product. The coal-tar is first stirred up energetically with lime-water in any convenient vessel, after which the mixture is allowed to stand until the coal-tar has subsided to the bottom, when the lime-water is drawn off. The tar is then well washed by decantation with hot water, and rectified in the ordinary naphtha still. Afterwards it is run into a long iron cylinder, which is placed over a furnace, and supplied with numerous large burners. Each burner has a metal funnel placed immediately above it, connected with a cast-iron pipe, into which all the fumes from each burner are conducted. The naphtha in the cylinder is heated almost to the boiling point by the furnace beneath. A series of smaller pipes lead away the fumes from the main pipe into a row of chambers, and thence into a series of large canvas bags, placed side by side, and connected alternately at top and bottom. The bags vary in number from fifty to eighty, the last one being left open to allow the smoke to escape, after traversing some 400 yards since leaving the burners. The best quality of lamp-black is found in the last bags, that near the furnace being much coarser and less pure. The bags are emptied whenever they contain a sufficient quantity.

The process employed in Germany for the manufacture of lamp-black is to conduct the products of the combustion of any resinous matter in a furnace into a long flue, at the end of which is placed a loose hood, made of some woollen material, and suspended by a rope and pulley. The lamp-black collects in this hood, and, when a sufficient quantity has accumulated, is shaken down and removed. In this manner about 6 cwt. of lamp-black may be collected in twenty-four hours.

One form of the apparatus is shown in Fig. 6. The circular structure *a* is lined inside with hanging cloths upon which the black can condense, and is covered with a

conical roof from which depends a movable sheet-iron cone *b*, perforated at its apex to give egress to a current of air. This cone *b* is supported by a rope *g* passing over a pulley *c*

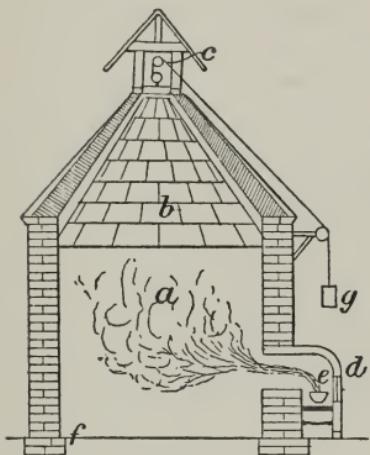


Fig. 6.—APPARATUS FOR  
MAKING LAMP-BLACK.

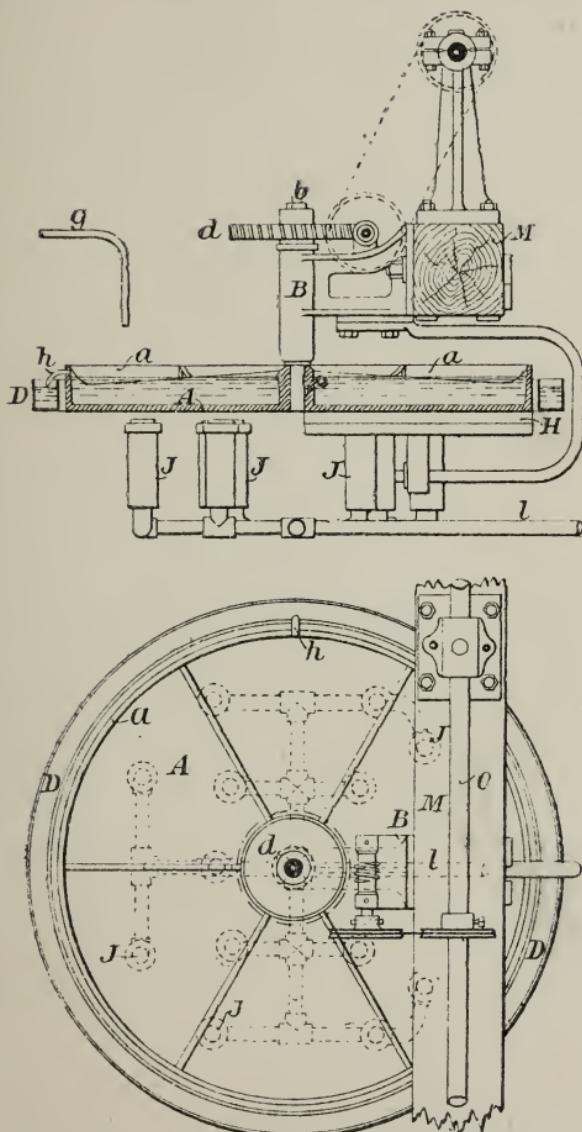
not ignite on contact with the air. The cone *b* is then lowered, and in its descent scrapes the walls of the chamber *a* and causes the black to collect on the floor, whence it is removed through an iron door *f* which at other times is kept tightly luted.

In England, an inferior variety is sometimes obtained from the flues of coke-ovens. That known as *Russian lamp-black* is made by burning chips of resinous deal or pine wood, and collecting the soot formed; but it is objectionable, owing to its liability to take fire spontaneously when left for a long time moistened with oil.

A modified form of apparatus has been introduced by Thalwitzer, a German manufacturer, and is shown in Figs. 7 and 8. A vertical tube is provided at its upper end with a funnel, into which cooling water is poured and flows out through openings in the tube immediately above a circular plate of thin cast or wrought iron arranged horizontally and

accessible from the outside. A fireplace *d*, containing a small iron dish *e* for holding the resin, is built against one of the side walls of the structure in such a manner that it can be fired externally. The rate of combustion is regulated by a small sliding damper on the door of the fireplace. When the black has accumulated in the chamber *a* to such an extent that operations must be suspended, the fire is let out, and the chamber is left to cool entirely, so that the black may

secured at its centre to the tube. Round the periphery of this plate is a vertical rim of tin plate, at the top of which is



Figs. 7 and 8.—THALWITZER'S LAMP BLACK APPARATUS.

a pipe through which the cooling water runs into a gutter round the top of the cylindrical casing, the water being

carried off from this gutter by a pipe. The vertical tube is carried near its upper end in a bearing, and at that part is attached a worm-wheel geared into it by a worm driven by any suitable power. At the underside of the circular plate is fixed a scraper, the edge of which is formed with a strip of leather in contact with the lower surface of the plate. Opposite the scraper, at the bottom of the casing, is a burning lamp, which sucks up the oil for its consumption by a flat wide wick.

The operation is as follows:—The vertical tube is caused to revolve by the action of the worm-wheel, the circular plate thereby receiving a slow rotary movement; and a small stream of water being poured into the funnel at the top of the tube, this water passes down the latter and through the openings on to the circular plate, which is thus kept cool. The burning lamp filled with paraffin or other oil is brought as near to the circular plate as is necessary for the cooling of the flame and the most perfect extraction of the carbon, which, in the form of soot, attaches itself readily to the plate, owing to its coldness and to the condensation of the steam produced. The revolving plate presents continually to the flames a new and clean surface, in consequence of the lamp-black being scraped away by the scraper as soon as deposited, and brought away through a pipe or shoot into a collecting barrel.

The apparatus as shown in Figs. 7 and 8 consists of a round metal plate A, provided with a flange a, and fixed on a vertical shaft b supported by the bearing B, and carrying at its upper end a worm wheel d set in motion by a worm. The plate A is cooled by water admitted through a pipe g, and the flange a is provided with a discharge pipe h, through which the cooling water runs into the groove D, surrounding the whole apparatus. Underneath the plate A a number of lamps J are applied, which are fed with oil by a common pipe l. H is an oblique scratcher or blade, the working edge of which is formed by a strip of leather, and touches the lower surface of the plate A.

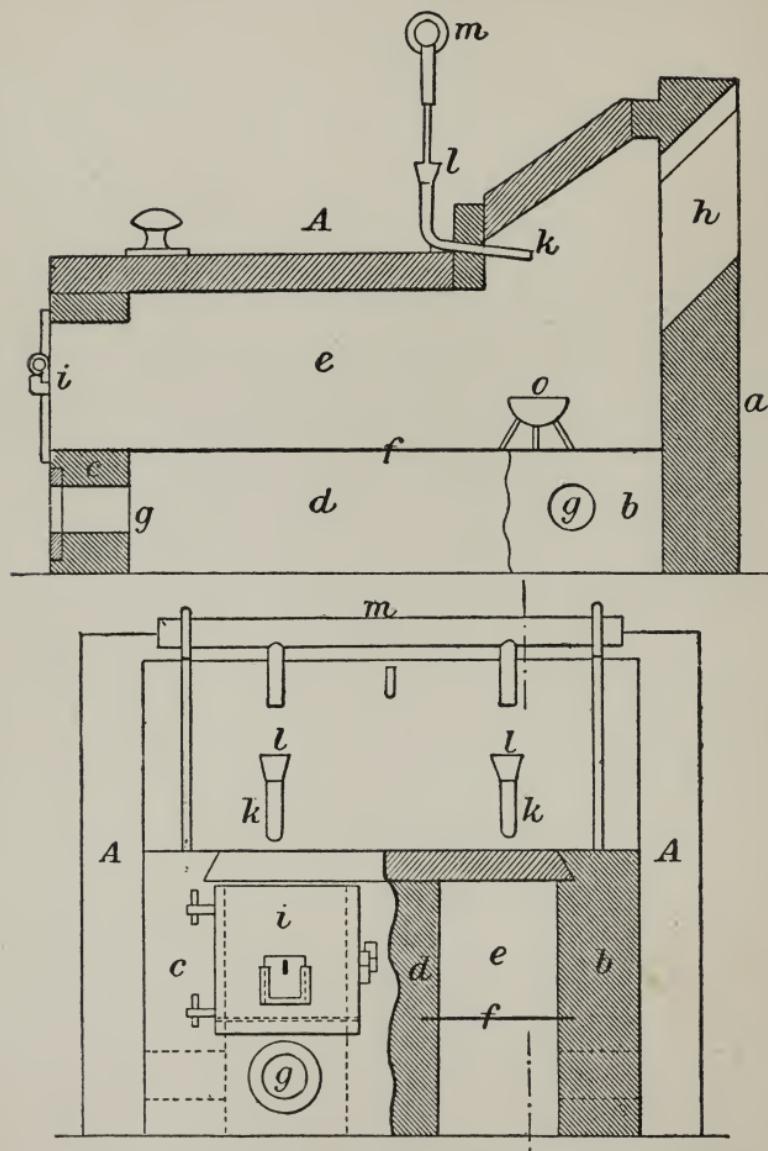
For manufacturing lamp-black, a slow rotary motion is imparted to the apparatus by means of the worm and worm-wheel, and a slight current of water is directed upon the plate A through the pipe *g*. The lamps J, filled with paraffin oil derived from lignite, or with any other suitable oil, are ignited and approached to the plate A as far as is necessary for cooling the flame, so as to deposit the greatest possible quantity of black. The latter adheres to the cold surface of the plate, which is also kept damp by the aqueous vapour formed during the combustion. The revolution of the plate serves to bring the flame continually into contact with new and clean portions of the plate, the black being continually scraped off by the blade or scraper placed opposite the flames, and conducted through a channel into a collecting trough.

There is a risk of overburning, causing a grey tint and a hard and granular texture.

A variety of lamp-black known as "carbon black" or "gas black," has of late years assumed an important position among black pigments. It is produced in considerable quantities in the United States by the combustion of the natural gas issuing from the earth in the mineral oil regions. The soot arising from the imperfect combustion of the gaseous hydrocarbon is made to deposit itself on cooled iron surfaces. These at first were made stationary, but now take the form of revolving discs or cylinders, which are automatically cleansed of the black as fast as it is deposited. This type of lamp-black is remarkably free from mineral impurities and unburned oil, and of a full colour.

An improved lamp-black kiln has been introduced in which the use of water is dispensed with. It is shown in Figs. 9 and 10. The furnace A, which is preferably built double, as shown, is constructed of brick lined with firebrick, with a rear wall *a* that divides the furnace room from the condensing room, side walls *b*, front *c*, and central dividing wall *d*, that divides the furnace into two long and narrow fire

spaces. The bottom of the fire spaces *e* is formed by a sheet iron plate *f* that is supported by the walls, and the space



Figs. 9 and 10.—AMERICAN LAMP-BLACK KILN.

below plate *f* serves as an air space through which air circulates by openings *g* in the front and side walls, this

circulation of air tending to keep the plate *f* cool. The rear of the fire space *e* extends upward and communicates by an opening *h* through the wall with the condensing room. In the front wall *c* is an opening to each fire space *e* and a door *i* to each opening. The oil or other liquid is supplied by pipes *k* that enter from the outside near the rear of the fire spaces. The outer end of each pipe *k* is fitted with a cup-shaped receptacle *l*, into which the oil will run from the vertical branch of the main supply pipe *m*, so that the amount of oil running into each pipe *k* may be observed, and regulated by a cock. The pipe *m* feeds the oil to one or more furnaces, the supply of material to each furnace being separately regulated. In the fire spaces beneath pipes *k* are placed shallow cast iron drip pans *o* to receive the oil, and the oil running in faster than it will burn will drop while on fire into the pans *o*, and be spattered into small particles. These pans are changed frequently, access to them being obtained by doors *i*. A slide *p* is provided in each door *i* to allow of ventilation when required. The slides and doors should close air-tight. By constructing the fire space *e* long and narrow, the plate *f* is more readily kept cool, and the space in front of the point of combustion renders the smoke less liable to escape by the doors. The products of combustion pass through the opening *h* to the condensing room, which is lathed and plastered, and if the room is sufficiently large a number of furnaces may be fitted to discharge into the same room. This furnace is especially adapted for burning dead oil; but by using burners of suitable construction other oils may be burned, and a superior quality of lamp-black made from mitigated spirits.

A very large proportion of the lamp-black now made is derived from the combustion of creosote or anthracene oils from coal tar, or of the residues of shale-oil distillation. The form of combustion chamber varies in different works, but is typified by the following rough sketch of that in use at the Stampshaw Chemical Works (Fig. 11).

At these works a horizontal brick flue *a* about 18 inches square and about 10 feet long is provided. At one end it enters the black-house *b*, and is here provided with a damper *c* to shut it off when not working. The other end opens to the air, and here is a sliding door *d* which, when shut down,

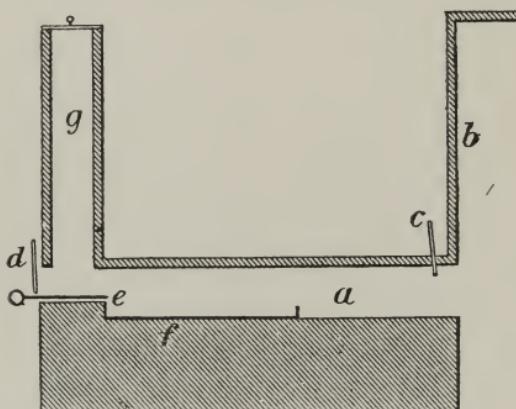


Fig. 11.—APPARATUS FOR MAKING LAMP-BLACK FROM CREOSOTE OR SHALE OIL.

leaves an opening round a small pipe *e*, which enters in this situation from a main pipe that conveys oil in a similar manner to four burners of this description placed side by side. At the bottom of the flue is an iron tray *f* to catch any liquid that falls from the tube, and in this tray the oil is burned. The burning of oil in one of these flues is not allowed to go on for more than three hours, and, when the combustion is over, the communication with the black-house is closed, the entrance door of the flue is opened, and the cover is taken off the chimney *g* so that the flue may become cooled, and another flue is taken into use.

The black-house is a brick chamber into which the smoke passes, and where it deposits its sooty particles. In some works there is only one undivided chamber; in other works there are more than one, and the chambers communicate by flues through which the smoke passes from one to another. At other works the chamber is divided by vertical

partitions, springing alternately from the two ends, so as to constitute one high zigzag flue, along which the smoke must travel to its outlet from the black-house. This chamber must needs have an opening somewhere to the outer air. The opening is sometimes a small chimney in the roof, and sometimes a short louvre tower. This is necessary to produce a trifling draught, just enough to carry the smoke into the chamber and no more.

In some works, the black from the black-house is also calcined, the object of the "calcination" being to get rid of all greasiness, a point of great importance when the lamp-black is to be used for making fine pigment. This process is conducted in circular iron pans, usually about  $2\frac{1}{4}$  feet high and  $2\frac{1}{4}$  feet diameter, which are provided with removable iron covers. A pan of this size will hold about 2 lb. of lamp-black. A bowlful is first put in and lighted by a red-hot iron; more and more is added from time to time as the ignition proceeds. When the pan, being full, leaves off smoking, the calcination is known to be complete, and the pan is then covered and its contents are allowed to cool. The loss undergone in this process is about 25 per cent. The smoke which comes off is acrid and very irritating to the eyes, like that proceeding from boiling oil, and it is difficult for a person unaccustomed to it to remain many minutes in the chamber where calcining is going on. This process is sometimes conducted within a chamber, but frequently under a shed or even in a building freely open to the air.

There are three sources from which nuisance may arise in lamp-black making: 1. The smoke which issues from the chimney of the black-house, small as it sometimes is, often constitutes a nuisance to near neighbours; but the nuisance is not a very serious one, and it does not extend very far from the works, never to a greater distance than about 50 yards. The odour, even when but little smoke escapes, is oppressive and suffocating in character, and resembles that

diffused in a room by a smoking table-lamp. It occasions headache, but is not otherwise injurious to health. 2. A similar nuisance of suffocating smoke sometimes proceeds from the burners, but this is when they are leaky or when there is a deficiency of draught through the black-house, or when the doors of the burning chambers do not shut closely, and when there is much wind blowing past them. This nuisance chiefly occurs when the burners are open to the air and merely protected by an open shed. 3. The escape of acrolein and other offensive vapours from the calcining house.

The best mode of preventing nuisance from the black-house is so to elongate the chamber as to give abundant opportunity for the soot to deposit in the course of the smoke along it to the outlet, and by taking means to consume by fire what little smoke escapes deposition. A most effectual arrangement for the accomplishment of these ends is to have a black-house 150 feet long, and so divided by partitions within as to cause the smoke to traverse a distance of altogether 500 feet before it finds an exit; the exit from the chamber communicating with a fire, in which the last of the smoke is consumed, and which serves to assist in regulating the draught through the chamber.

The regulation of the draught through the burner and black chamber is of importance in order to avoid the escape of smoke from the burners. If the draught be too great, too much black is lost from the chamber, but if, on the other hand, it be too little, the smoke instead of passing into the chamber will come out into the works and create a nuisance, especially where the burners are erected in the open air, under circumstances in which variation in the force of the wind cannot fail to interfere with due regulation of draught. This part of the manufacture should be conducted within a building of some sort.

The best mode of preventing nuisance from calcination is in operation at Shackell & Edwards' works, in Hornsey Road, Islington. At these works the black is calcined in a chamber

20 feet square and 25 feet in greatest height, with a paved floor and arched roof. In the centre of the roof is the opening where a fire was formerly placed, but which is now closed by a sky-light, capable of being raised. The calcining pots are ranged round this chamber, and a fan, employed to draw off the vapours from the oil-boiling pans, is further utilised to draw off also, from the upper part of the calcining-house, the vapours arising from the calcination, and to drive them into the boiler fire, where they are consumed. Calcination should always be conducted in a closed building duly ventilated so as not to create nuisance.

The transport of lamp-black is effected in barrels or bags; when in the latter, these should be previously soaked in water containing some clay in suspension, which stops up the pores of the sacking, and thereby prevents loss.

The particular virtue of lamp-black as a pigment lies in its state of extremely fine division, which could not possibly be attained by artificial means; this quality renders it invaluable as the basis of black pigments, all of which contain it in a greater or less quantity. Indian ink and printers' ink are also composed principally of this substance.

**Unimportant Blacks.**—In addition to the recognised blacks already noticed there are a number of other sources of black pigment which have been drawn upon to a limited extent, or have been suggested as substitutes for the standard articles. They only merit a short description.

*Aniline black* is prepared by adding an acidified (sulphuric) solution of bichromate of potash to an aqueous solution of hydrochlorate of aniline, and washing the precipitate. The cost is prohibitive.

*Candle black* is candle smoke condensed on a cold plate.

*Charcoal black* is finely-ground wood charcoal.

*Coal black* has been suggested by grinding coal, but lacks the requisite qualities of a pigment.

*Cork black* is a very fine pigment prepared by calcining cork refuse. Limited supply.

*German black* is Frankfort black.

*Iron black* is ground black sulphide of iron.

*Lead black* is prepared by boiling lead fume in sulphide of soda solution. It would probably be unstable on account of oxidation.

*Manganese black* is ground oxide of manganese. It is costly, and dries too quickly.

*Prussian black* is calcined Prussian blue. It is not of a good colour, nor economical.

*Prussiate black* is the carbonaceous residue from making yellow prussiate of potash. Used chiefly for decolorising syrups, &c.

*Spanish black* is cork black.

*Tannin black* is proposed to be made by exhausting the tannin from refuse leather and tanning agents, and adding alum and sulphate of iron. The colour is blue-black, weak, and unstable.

## CHAPTER III.

## BLUES.

**Cobalt Blues.**—Some of the compounds of cobalt with alumina, phosphoric acid, silica, and tin, are remarkable for possessing a fine blue colour of great permanency and indestructibility, and still find a limited application. They are chiefly as follows:—

Cœruleum—a mixture of the oxides of cobalt and tin.

Cobalt blue—a mixture of the oxides of cobalt and alumina.

Smalts—a double silicate of cobalt and potash.

**CŒRULEUM.**—This is a light-blue slightly greenish colour, with no purple tendency in artificial light. It is non-granular, covers well, mixes with water or oil, and is a good artists' colour for sky effects. It is permanent in strong sunlight and impure atmosphere, and resists acids and alkalies at normal temperatures. Hot hydrochloric acid dissolves it, and addition of water to the pale blue solution produces a violet red; evaporation to dryness restores the original pigment. The green tint of a nitric acid solution is due to iron and nickel impurites. Dilute sulphuric acid causes partial decomposition of cœruleum, but it is proof against caustic potash, acetic acid, and concentrated sulphuric acid. Its composition is given as

Cobalt oxide .. .. .. .. .. ..	18·66
Tin oxide .. .. .. .. .. ..	49·66
Silica and sulphate of lime .. .. .. .. ..	31·68
	100·00

There are several methods of preparing coeruleum :—

(1) A solution of stannate of potash is added to one of cobalt. A blue precipitate is thrown down, which, on washing, becomes first light-red and then brown. When calcined at a white heat it assumes a blue colour.

(2) A solution of stannate of soda is mixed with a solution of nitrate of cobalt, and the resulting precipitate calcined to bright redness forms a blue pigment.

(3) Solutions of cobalt and tin are mixed and precipitated by soda, the precipitate washed free from soda being calcined as in all the other cases. The silicate of soda is the most satisfactory sodium salt for a precipitant.

**COBALT BLUE.**—This rich pure blue pigment is not alone permanent, but actually develops its full intensity only after exposure to the air. With age, however, it acquires a greenish tendency, and in artificial light it inclines to a violet tint. It is proof against acids and alkalies, and mixes particularly well with water. In combination with other pigments it is unaltered and has no effect on them. Its tones are different from those of ultramarine. It slowly decomposes when heated in strong sulphuric acid, yielding a violet solution and a white precipitate, which latter dissolves and affords a blue liquid on dilution with water. It consists principally of about 80 per cent. alumina, and 15 per cent. oxide of cobalt.

There are several ways of preparing it :—

(1) By Thénard's original process, roasted cobalt, from Tunaberg, Sweden, is dissolved under heat in an excess of nitric acid. The solution, evaporated nearly to dryness, is boiled in water, and the deposit of arseniate of iron is filtered out. Into the filtrate is poured a solution of basic phosphate of soda, which throws down a precipitate of basic phosphate of cobalt, varying in hue from violet to pink. This precipitate is washed on a filter, and, while still gelatinous, 1 lb. of it is intimately mixed with 8 lb. of hydrated alumina, recently precipitated by ammonia from a solution of potash-

alum. The mass is first dried to brittleness and then calcined in a covered clay vessel for half an hour at a cherry-red heat. The resultant blue pigment is stored in glass receptacles.

The preparation of the gelatinous alumina is conducted as follows. The potash-alum is dissolved in at least three times as much water as is necessary, and is then precipitated by an abundant excess of ammonia, with frequent stirring. When settled, the supernatant liquor is siphoned off, and the precipitate is thoroughly washed several times on a filter.

Thénard blue will vary in tint according to the proportions of alumina used. A pure colour is obtained with 4-5 parts alumina to 1 of phosphate of cobalt; a greenish hue with equal parts of alumina and cobalt salt; and almost any intermediate tone by varying the proportions between these limits.

(2) To 16 parts of gelatinous alumina add 1 part of arseniate of cobalt, obtained by precipitating the solution of cobalt by arseniate of potash.

(3) A richer and more velvety blue is got by using oxide of cobalt and substituting phosphate of lime for the alumina (Boullai-Marillac).

(4) Binder's process is as follows:—Dissolve by boiling 6 lb. alum, free from iron, in a leaden or earthenware vessel, and filter it into a vat  $5\frac{1}{2}$  ft. high and 3 ft. across, one-third full of clean water. Precipitate the alumina by solution of potash, fill up the vat with water, settle, decant the clear liquor, and wash repeatedly till barium chloride gives no precipitate. Dissolve  $\frac{1}{2}$  lb. sesquioxide of cobalt in  $1\frac{1}{2}$  lb. hydrochloric acid at  $22^{\circ}$  B., and evaporate to dryness. Dissolve the residue in 3 lb. hydrochloric acid, and pass a stream of sulphuretted hydrogen through it, to throw down any foreign metals. Filter clear, evaporate again to dryness, and dissolve the residue in enough water to produce  $4\frac{1}{2}$ -5 lb. of solution. Next precipitate the cobalt solution (3 to 6 lb., according to depth of tint required) by ammonia, avoiding

excess. Wash the precipitate, and add it to the water, holding the gelatinous alumina in suspension, stirring thoroughly for  $\frac{1}{2}$  an hour. A reddish tint in the supernatant liquor shows that some of the cobalt has been dissolved. Add a little ammonia, and allow the precipitate to settle. Decant and add new waters repeatedly. Finally collect on a fine filter cloth, drain, press, stove dry, and calcine for  $2-2\frac{1}{2}$  hours at red heat in clay crucibles; then cool, grind first in a mill and then on a slab, and sift.

SMALTS.—This pigment has not maintained its position in competition with artificial ultramarine. Formerly it was very largely used to correct the yellow tone of cottons, papers, and pottery. It has a pale violet-blue tint, which, however, is not constant in artificial light. Being a silicate it is very permanent, and proof against the action of acids, alkalies, and sunlight, besides being inert when mixed with other pigments. It can be used with either water or oil as a medium, but is not a successful paint owing to its weak colouring power. It is virtually a double silicate of cobalt and potash, or a cobalt glass, containing a few impurities, of which the chief are aluminium, iron, and lead oxides. The colour varies somewhat according as these impurities fluctuate, and the finest ground sample is always the palest. It is hardly ever adulterated, and the chief point to secure is that it be ground to the finest possible degree.

Its manufacture is most extensively and successfully carried on in Saxony. The raw materials used are cobalt speiss (an arsenide of cobalt and iron), potash, and sand. The ore is broken up into convenient sized pieces and roasted at red heat in a reverberatory furnace provided with a tall shaft for discharging the sulphurous and arsenical fumes at a high altitude. When the evolution of these fumes has ceased and the mass begins to assume a pasty consistence, the roasted ore is removed from the furnace, cooled, reduced to a fine pulverulent condition (then known as "zaffre") and passed through a silken sieve. Should it be necessary,

the cobalt ore is first spalled and hand-picked to remove the ores of foreign metals which are associated with it; and then reduced to a very fine state in an edge runner or mortar mill, and freed from earthy impurities by washing. The concentrated ore is then dried and dead-roasted in small charges at a time (about 4 cwt.) in a specially designed reverberatory furnace such as shown in Fig. 12, of which *a*

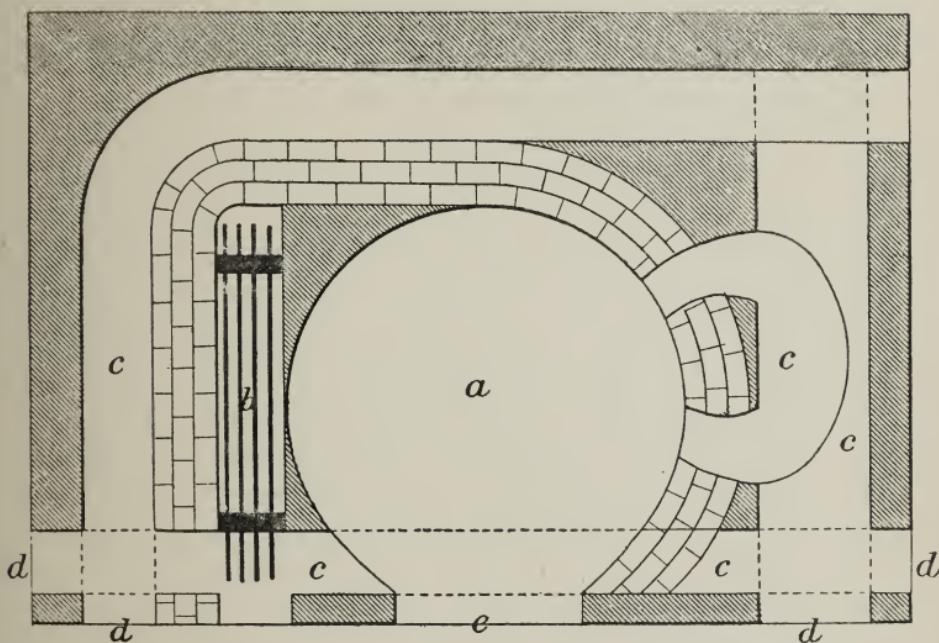


Fig. 12.—FURNACE FOR ROASTING COBALT ORES.

is the hearth on which the ore is spread; *b*, the fireplace, the products of combustion from which pass over the ore on the hearth, and thence into the flues *c*, which repeatedly circle round the furnace so as to provide abundant opportunity for the arsenious oxide derived from the combustion (oxidation) of the arsenic in the ore to condense; this highly poisonous arsenious oxide is collected in a solid form from the flues at convenient intervals by means of the doors *d*. The ore is charged and discharged at the door *e*. The

roasting should not be carried to such a point that the whole of the sulphur and arsenic are removed when making smalts, as by leaving a portion of these substances in the ore at this stage, the ultimate purification is better accomplished.

The next stage is to fuse the roasted ore with potash and silica so as to form a blue glass. The proportions in which the ingredients are mixed depend upon the depth of colour in the zaffre operated upon and the tint desired in the finished smalts; hence it is always determined by a preliminary experiment, and is then most carefully adhered to, each material being accurately weighed out. Only the best potash can be used, as it must be quite free from soda, and iron or other metal; the effect of soda is to render the blue greenish tinted. Quartz affords the requisite silica, and is hand-picked to ensure freedom from alumina, iron, and lime, which import dullness into the colour, and then ground to a fine powder in an edge runner mill. The duly weighed quantities of the several ingredients are intimately mixed in wooden or cement lined vessels, so as to preclude the possibility of any metallic iron finding its way in; and as a further protection against this risk a little white arsenic is often added so that the iron may be carried down in the regulus which is formed during the fusion in the crucible.

These crucibles are of refractory earthenware quite free from lime, and measure about 18 inches across at top, gradually diminishing to 14 inches at bottom, so that an ordinary charge is about  $\frac{3}{4}$  cwt. They are placed in rows in a furnace which generally bears a close resemblance to a glass furnace, the operation being very similar. The form of furnace common in Saxony, where most of the smalts is made, is shown in Fig. 13. By means of a series of openings *a* in the walls of the furnace the pots *b* are introduced on to the hearth of the furnace, whereupon the openings *a* are bricked up again and remain closed during the operation. The ingredients are charged into the pots *b*

by means of long iron ladles which are introduced through the small square apertures *c*, which can be temporarily closed by a half-brick or other simple article. The fire is then lit in the fireplace *d*, and the products of combustion circulate around the pots *b*, and finally escape at the orifices *e*

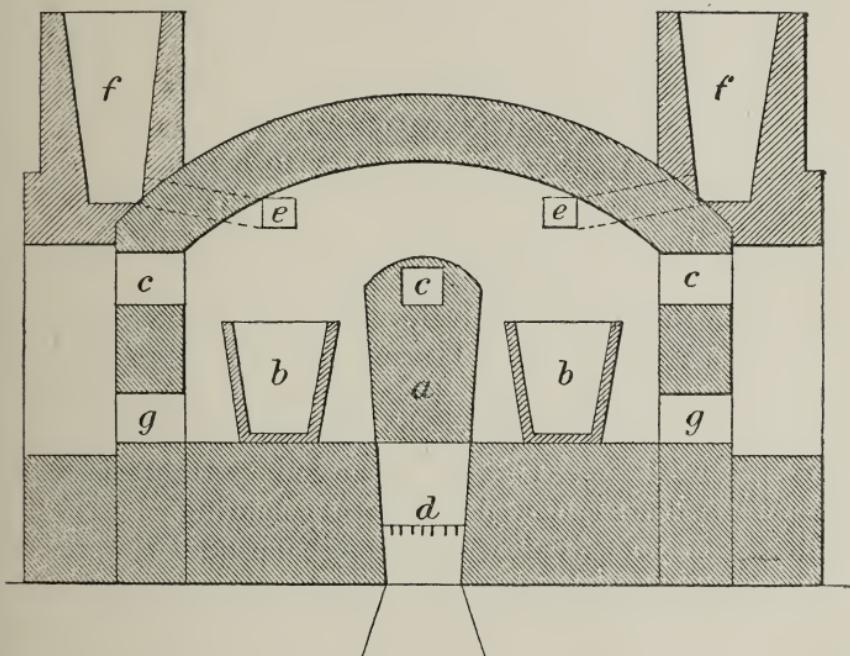


Fig. 13.—FURNACE FOR MAKING SMALTS.

at the top of the furnace into flues leading to the chimney *f*. After about 8 hours' firing fusion commences in the pots, whereupon the contents are thoroughly stirred by rods inserted through the working holes *c*. The temperature is then increased till a white heat is attained, this being necessary for the formation of a glass. The fused mass is repeatedly sampled, and when it has become quite homogeneous, and the regulus or speiss containing the iron, antimony, bismuth, arsenic, copper, nickel, sulphur and other impurities has completely separated itself and collected

at the bottom of the pots, the blue glass is ladled out and dropped at once into cold water, by which it is disintegrated and rendered very brittle ready for the subsequent grinding. The regulus is then drawn off from the pots through holes provided for the purpose, and removed by the orifices *g*, after which the pots are ready for another charge. They ordinarily remain serviceable for about six months.

The grinding needs to be done with great thoroughness, and is accomplished partly by stamps and partly by edge-runner mills in the presence of water. The particles as reduced are floated off by the water to a series of settling tanks communicating one with another. The portion which settles in the first of the series is too coarse for use, and is returned to the edge-runner for further grinding; while the portion in the last of the series possesses such a weak colour that it is rejected, or put into the crucible to undergo a second fusion. The selected portions are dried ready for the consumer.

**Copper Blues.**—These form an unimportant class, being unstable and not endowed with great colouring power. Their tint is pale and greenish, and though opaque in water, they are not particularly so when mixed with oil. Exposed to the action of sulphur or its compounds, whether present as sulphuretted hydrogen in the air, or in combination with a metal, forming another pigment with which they may be mixed, copper blues undergo an important chemical change, the carbonates and oxides of copper being converted into the sulphide, which is black. Under the influence of heat too the blue carbonate will lose its carbonic acid, and be turned into the black oxide. Ammonia and the acids dissolve them, but other alkalies are resisted until heat is applied. The chief kinds of copper blue are Bremen blue, cæruleum, lime blue, mountain blue, Péligot's blue, and blue verditer.

**BREMEN BLUE.**—This is a more or less pure hydrated oxide of copper, varying in its qualities according to the method of preparation. When made by precipitating a neutral salt

of copper from solution, it forms a dense and compact mass; whereas a porous and pulverulent pigment results when basic and insoluble copper salts are treated with alkalies.

(1) The foundation of the manufacture of this colour was waste copper scrap, such as ship's sheathing, from which, in various ways, was prepared a basic chloride or oxy-chloride. Some of the methods adopted were:—(a) 100 lb. scrap copper, 99 lb. powdered sulphate of potash, and 100 lb. salt, moistened with clean water; (b) 100 lb. copper fragments, 60 lb. salt, and 30 lb. diluted sulphuric acid (3 volumes of water to 1 of acid); (c) a solution of copper oxide (scales) in pure hydrochloric acid poured over the scrap copper. The method (a) produces a chloride of copper which, in contact with more metal, becomes a sub-chloride; this, absorbing more oxygen from the air, is converted into the basic green "oxide" of the factories. By the (b) process, the hydrochloric acid set free, and the atmospheric oxygen produce the same result. In the (c) process a similar effect is obtained.

It is of primary importance that no trace of this sub-chloride of copper shall be allowed to remain, as it undergoes decomposition by caustic alkalies, and throws down an orange-yellow sub-oxide of copper. Hence it has sometimes been the practice to prepare the basic oxychloride twelve months in advance, and to stir it frequently before use. Complete oxidation, however, can be satisfactorily accomplished by alternately wetting and completely drying the mass.

An interesting phenomenon takes place during the transformation of this green magma into a hydrated oxide of copper. On this magma being introduced by degrees into a caustic potash or soda lye of about 22° B., the thoroughly washed and dried product is exceedingly fine, with great covering power, and deepens on addition of a little water. When the magma is diluted with an equal volume of water, and the mixture at once poured into an excess of caustic lye,

with constant agitation, a few minutes' rest will suffice for the mass to assume a most compact consistence. The colour thus produced, when washed and dried, is much lighter in colour, and has less body. A blue derived from any of these products is unsatisfactory as regards freshness and intensity of colour; whereas by adding a small quantity of concentrated solution of sulphate of copper to the magma before treating it with the alkaline lye, apparently a highly basic sulphate of copper is produced which deepens the colour.

A pigment with good body can be made in the following manner. To 100 lb. of the thick magma of basic oxychloride add a concentrated solution of 7 lb. sulphate of copper, and then 40 lb. of a concentrated caustic lye ( $32^{\circ}$ - $36^{\circ}$  B.), with vigorous and rapid stirring, finally adding about 150 lb. of caustic lye at  $20^{\circ}$  B. When the decomposition is quite complete, the precipitate is carefully washed, passed through a fine hair sieve, and filtered. Drying is effected at a low temperature, to ensure that the hydrated state of the oxide is not changed; and the air of the drying chamber must be free from acid or sulphuretted vapours.

(2) If neutral nitrate of copper be decomposed by an insufficiency of potash carbonate solution, the flocculent precipitate of copper carbonate resulting is by degrees transformed into a sub-nitrate of copper, which goes down as a heavy green powder. On treating this sub-nitrate with a potassic solution of zinc oxide, a dark-blue coloured pigment is formed, which is apparently a zincate of copper mixed with a very small proportion of a highly basic nitrate of copper. Though very light it has great covering power. In practice the manufacture is conducted as follows.

Calcine copper scales in a reverberatory or muffle furnace till the sub-oxide is entirely converted into protoxide, or until it dissolves in nitric acid without evolving red nitrous fumes. Heat is applied to the solution of nitrate of copper, which is decomposed by addition of a clear solution of potash

carbonate. After effervescence has subsided, small doses of potash carbonate solution are added till but little undecomposed copper is left. This residue is recovered by decanting the clear liquor, and repeatedly washing the green precipitate with small quantities of clean water, collecting all the washings, and finally precipitating by potash solution. On introducing the green carbonate of copper into a new solution of copper nitrate, it is transformed into a basic salt. Crystals of nitrate of potash are obtained by evaporating the previous liquors.

To obtain an economic solution of zinc oxide, clippings of metallic zinc are treated with a solution of caustic potash or soda in a cast-iron vessel. The immediate result is a disengagement of hydrogen, and saturation of the alkali with zinc oxide, which behaves as an acid. The cleared liquor serves for decomposing the basic nitrate of copper. The pigment produced is a handsome blue, and the potash liquor can be evaporated down till it yields crystals of saltpetre. The economy of this method lies in producing nitric acid cheaply from soda nitrate and obtaining saltpetre as a bye-product.

(3) An inferior and cheaper pigment is made in the following manner. To a solution of copper sulphate add one of barium or calcium chloride till a white precipitate ceases to go down, and from the cleared blue liquor all the copper is precipitated by addition of fresh milk of lime. Usually the weight of quicklime required is 20 per cent. of the copper sulphate. The settled, washed, and dried precipitate is the pigment desired. The cleared barium or calcium chloride solution may be used anew as a precipitant for the next batch.

CÆRULEUM.—This name has been given to the beautiful blue pigment used in Egyptian and Pompeian mural paintings, and exhibiting the same bright blue after 1000 years' exposure to the weather as when first used. Its composition has been given by Fouqué as approximately  $63\frac{1}{2}$  per cent.

silica, 21 per cent. copper oxide, and 14 per cent. calcium oxide, and he regards it as a double silicate of copper and calcium. It is supposed to have been produced by fusing together copper ore, sand and lime, but experiments have not yet resulted in a successful imitation of the pigment, a difficulty being encountered in the fact that if too high a temperature be permitted, destruction of the blue colour ensues, and a green glass results instead. This is unfortunate, as its remarkably bright and stable hue would make it very popular if it could be manufactured at a moderate cost. It withstands sulphuretted hydrogen, and even prolonged boiling with any of the acids or alkalies.

LIME BLUE.—This pigment is essentially a mixture of hydrated oxide of copper and calcium sulphate. It resists the action of alkalies in the cold, but turns black when boiled in caustic soda, and is completely soluble in hydrochloric acid. Ultramarine has largely, if not entirely usurped its place. There are several ways of making lime blue :—

1. Any soluble copper salt the acid of which will make a soluble salt with lime is suitable, the only precaution necessary being that if in the decomposition of the copper and lime salts, the combination of the whole of the sulphuric acid with the lime is not attained, there should be an excess of copper sulphate in the liquor rather than of the lime salt. The resulting copper solution, containing very little lime sulphate, is settled in a cool place for 24–36 hours, filtered, and diluted with clean water down to about 18° B. Meantime a milk of lime is prepared with very white and well-burned lime, slaked and mixed with abundance of pure water, and kept stirred for a long time in a lead-lined vat. After a short rest to permit sand, &c., to precipitate itself, the milk is drawn off, and left to settle in lead-lined or copper pans. The deposit is collected, ground in a mill where contact with iron is impossible, and passed through a very fine sieve.

The mixture of lime and copper solution is made in the proportion of 100 lb. dry lime with 175 dry copper salt, if the most intense coloration is desired, but the proportion of lime may be much increased without detriment to the pigment beyond lessening its intensity of colour. After complete settlement of the precipitate, the clear liquor is decanted; the pigment is carefully washed with clean soft water, and drained on filter cloths till it is of a convenient consistence forming a green paste. A definite weight of this paste calculated on the dry pigment is taken for further incorporation, consequently it is first necessary to ascertain how much water is in the paste. Usually it amounts to 75 per cent., and on this basis 5 lb. of the paste are stirred up with 1 gal. clean water in a lead-lined vat, with addition of  $\frac{1}{2}$  lb. wet lime under constant agitation. Subsequently  $\frac{1}{4}$  pint of clear solution of best potash at 15° B. is well stirred in, and the mixture is immediately taken to the mill and most thoroughly ground.

Further, for each 10 gal. of green paste is prepared a clear solution of 1 lb. pure salammoniac in 2 gal. water and another solution of 2 lb. copper sulphate in 2 gal. water. The liquid paste is drawn off from the mill into a stoneware vessel, and the two solutions of salammoniac and copper sulphate are immediately added. After complete agitation and combination, the mixture is left for 4 or 5 days to settle, and turned into a lead-lined vat, where it is repeatedly washed with clean waters until turmeric paper is not discoloured.

(2) Precipitation of copper sulphate by excess of thin milk of lime in the cold, followed by washing and drying, will give a lime blue which will dry without turning black. Or 100 lb. of the copper sulphate may be treated with a milk of lime prepared from 30 lb. quicklime and addition of  $12\frac{1}{2}$  lb. salammoniac. When the liquor has become colourless, the pigment is prepared from the precipitate; but the lime should be ground after slaking, and the milk of lime left to stand for some days before use. The salammoniac seems

to be essential to the production of a pure full blue. Milk of lime poured drop by drop into the ammoniacal copper solution gives a precipitate which redissolves on agitation, and remains long in solution under heat, but finally throws down a permanent precipitate, while the liquor on standing gives beautiful blue crystals. From experiments it appears that out of seven atoms of copper sulphate in the liquor, five are precipitated by milk of lime and the last two are decomposed by ammonia. A greater proportion of lime will produce a precipitate holding a certain quantity of less valuable pigment. A smaller proportion of lime yields a finer coloured and more crystalline pigment, because it crystallises partly in the excess of solution, so that by incomplete decomposition a smaller yield of superior pigment is obtained. The proportions necessary for formation of the colour are 7 equivalents of copper sulphate, 5 of lime, and 2 of ammonia, and if the 2 equivalents of ammonia be replaced by 2 of lime and 2 of salammoniac, the proportions furnishing the best colour will be 100 lb. copper sulphate, 24 lb. lime, and  $22\frac{1}{2}$  lb. salammoniac.

Both caustic soda and caustic potash produce a fine blue precipitate in a solution of ammoniacal copper sulphate with excess of ammonia, but the liquor decolorises only on evaporation of the ammonia. The precipitate becomes lighter-hued the more it is washed, and consists of hydrated oxide of copper with a little carbonic acid; it does not turn brown even when heated in presence of excess of potash or soda. Moreover the presence of ammonia renders the hydrated oxide of copper much more permanent. The composition of this pigment is given by Gentile as  $33\frac{1}{2}$  per cent. copper oxide,  $23\frac{1}{2}$  sulphuric acid, 16 lime, and the remainder water, &c.

MOUNTAIN BLUE OR AZURITE.—This natural blue pigment consists essentially of a basic carbonate of copper, and is found in quartz rocks in England, France, Bohemia, Hesse, Saxony, the Tyrol, and Siberia. It affords a rich sky-blue

paint of a permanent character, but being comparatively costly is not largely employed. Its composition is about 69 per cent. copper oxide,  $25\frac{1}{2}$  carbonic acid, and 5 water. The only preparation needed is exceedingly fine grinding.

PÉLIGOT BLUE.—(1) Whereas the hydrated oxide of copper precipitated from a solution of a salt of copper by excess of potash or soda rapidly blackens even though washed with cold water, Péligot obtains a blue hydrated oxide which resists boiling and heating at  $212^{\circ}$  F. He uses any soluble copper salt, but preferably the sulphate. A very dilute solution of the copper sulphate is treated with ammonia in excess (*aqua ammoniæ* or an ammoniacal salt) and precipitated by soda or potash.

(2) On adding water in excess to a slightly ammoniacal solution of copper nitrate, the same pigment is obtained.

(3) A mixture of 73 parts silica, 16 oxide of copper, 8 lime, and 3 soda, is fused together at a temperature not much exceeding  $800^{\circ}$  F. At higher temperatures there is risk of the pigment turning black.

VERDITER.—This sky-blue and not very durable pigment, used in water-colour painting, closely resembles Bremen blue (see p. 34) in composition and manufacture. It consists chiefly of copper carbonate, mixed with a lesser proportion of hydroxide, sulphate, or oxide, and occasionally a small quantity of sulphate of lime; and is most satisfactorily prepared from copper chloride or nitrate, though almost any salt of copper may be used. The mode of fabrication varies.

(1) To a solution of the nitrate or sulphate is added one of potash or soda carbonate so long as any precipitate is formed, and this precipitate, when filtered and washed, is treated with a weak caustic soda solution.

(2) A hot solution of chloride of lime is added to a hot solution of sulphate of copper at  $62\frac{1}{2}^{\circ}$  Tw. till the precipitate ceases to go down. The solution of chloride of copper which constitutes the liquor is filtered off, diluted with water to

about  $31\frac{1}{2}$ ° Tw., and treated with repeated small doses of slaked lime ground exceedingly fine in water till no more copper is precipitated. The resulting green paste is drained, filtered, washed, and put into wooden vats; here 8 lb. of lime paste and 5 pints of potash carbonate solution at  $25\frac{1}{2}$ ° Tw. are added for every 70 lb. of *dry* colour contained in the green paste, the whole mass being thoroughly agitated, then allowed to rest till the development of the required shade is accomplished, when it is filtered, washed, and dried.

(3) In some German works the final green paste as prepared in (2) is put into air-tight vessels, and a solution of 3 lb. ammonium chloride and 4 lb. sulphate of copper in 7 gal. of water is introduced for each 70 lb. of *dry* colour in the green paste. After complete admixture of all the ingredients, the receptacles are fastened up for several days so that the reactions may proceed out of contact with the air, and finally the pigment is removed, washed, and dried for use.

**Indigo.**—The well-known blue colouring matter termed indigo is produced by a great number and variety of plants, distributed throughout all the tropical countries of the globe. Commercially, it is obtained chiefly from species of *Indigofera*, as *I. tinctoria*, the cultivated species of India, furnishing the chief article of commerce, found also in Madagascar, St. Domingo, &c.; and *I. Anil*, in the Punjab, W. Indies, and on the Gambia river. Some is also obtained from *I. argentea*, in Africa and America: *I. Caroliniana*; *I. disperma*, the cultivated plant of Spain, America, and some of the E. Indies; *I. cærulea*, the “black indigo” of India; *I. glauca*, in Egypt and Arabia; *I. pseudo-tinctoria*, cultivated in some parts of the E. Indies, and said to yield the best dye; *I. cinerea*, *I. erecta*, *I. hirsuta*, and *I. glabra*, in Guinea. Considerable local supplies are obtained from the following plants:—*Isatis tinctoria*, in Europe and China (see Woad); *I. indigotica*, cultivated in some parts of China; *Amorpha fruticosa*, in Carolina; *Baptisia tinctoria*, wild, in the United States; *Gymnemia (Asclepias) tingens*, in Burmah; *Polygala tinctoria*,

in Arabia ; *Polygonum Chinense*, *P. tinctorium*, *P. perfoliatum*, *P. barbatum*, *P. aviculare*, in China and Japan, and introduced into Belgium ; *Ruellia indigotica*, largely cultivated in Assam, as well as in India, and at Che-king, in China ; *Tephrosia tinctoria*, and *T. apollinea*, in India and Egypt ; *Wrightia tinctoria* (*Nerium tinctorium*), the Palas indigo of the Carnatic.

The cultivation of indigo (chiefly *Indigofera tinctoria*) is very extensively carried on in India, especially in the district included between 20° and 30° N. lat. The soil best suited for the culture is a rich loam, with a subsoil which is neither too sandy nor too stiff; alluvial soils give the best returns, but good crops are sometimes raised on higher grounds. The land is ploughed in October–November, after the rains; the seed, about 12 lb. to the acre, is sown in February–April. Too rapid growth diminishes the yield of dye. In July–September, the plants are in full blossom, and the harvest takes place. The preparation of the dye-stuff may be performed in either of two ways, which are distinguished as the “dry-leaf,” and the “green-leaf” process. The latter is considered the better, and is the more general; it is conducted as follows:—The flowering plants are cut down at about 6 in. from the ground, and immediately taken to the steeping vats, within which they are spread out and pressed down by beams fitted to the side posts of the tanks. Enough water is then admitted to cover the plants; if this be delayed, fermentation may set in and spoil the product. The duration of the steeping is liable to considerable modification, and needs much judgment and experience; with a temperature of 96° F. in the shade, 11–12 hours may suffice; in cooler weather, 15–16 hours may be necessary. Moreover, very ripe plants require less time than young and unripe ones. The following general conditions indicate the time for suspending the maceration :—(1) The sinking of the water in the vat; (2) the immediate bursting of the bubbles that arise; (3) an orange tint mingled with the green, when

the surface water is disturbed ; (4) the emission of a sweetish, pungent odour, quite distinct from the raw odour of the unripe liquor. At this point, men enter the vat, and stir up its contents either by hand or by a wooden paddle. The agitation is at first gentle, but increases as the fecula begins to separate ; this is known by the disappearance of the froth, and by the colour of the liquor changing from green to blue. The "beating," as it is called, is continued for  $1\frac{3}{4}$ -3 hours, the following conditions being a guide as to its sufficiency :—(1) The ready precipitation of the fecula from a sample of the liquor, and the madeira-wine colour of the latter ; (2) a brownish colour observed on dipping a cloth into the liquor, and wringing it out ; (3) the appearance of a glassy surface on the liquor, and the subsidence of the froth with sparkling and effervescence.

Next a little pure cold water, or weak lime-water, is sprinkled over the surface of the liquor, to hasten the settlement of the fecula, which occupies 3-4 hours. After this, the water is drained away from the top, by means of plug-holes in the side of the vat. The precipitated fecula is then removed to a boiler. Here it is made to boil as promptly as possible, and is kept boiling for 5-6 hours ; it is constantly stirred, and skimmed with a perforated ladle. After boiling, it is run off to a straining table, where it stays for 12-15 hours to drain ; next it is pressed for about 12 hours, and then cut, stamped, and placed to dry. The ordinary dimensions of a steeping-vat are 16 ft. by 14 ft. by  $4\frac{1}{2}$  ft. deep ; this will contain about 100 *maunds* (8200 lb.) of plants, which may yield from 40 lb. downwards of indigo. The beating-vat is less deep.

Such are the methods of cultivation and manufacture most generally in use throughout India. In limited districts, however, some modifications are in vogue. On land subject to inundation, the plants last only one year. South of the Ganges, the seed is sown at the beginning of the rains, and the plants remain on the ground for two years, thus giving a

double crop, the second of which is the larger and better. In very strong land, a third crop is sometimes secured. Occasionally, sesame is sown on the same ground, and harvested before the indigo is cut. Small quantities of indigo are grown on poppy lands, and irrigated. The seed is sown in March–April, and the crop is gathered at the end of the rains, in time for an opium crop to be taken off the land. Indigo is sometimes manufactured by collecting the fecula, and dropping it in cakes to harden in the sun ; this is “gaud” indigo, of very inferior quality. The fecula is improved by boiling it in coppers and pressing it into boxes. The production of the indigo blue is the result of the decomposition of the colouring principle of the plant, which exists as a glucoside. Plants grown on poor soils, and in dry climates, yield almost the whole of this glucoside to the ordinary process of steeping and beating described above ; but plants raised on rich alluvial soil, and in damp heat, contain an amount of glucoside which cannot be utilised by the ordinary process. In order to prevent this waste, which causes the richest plants to give the least return, it is necessary either to prolong the fermentation, and raise the heat to 95°–100° F., or to add a solution of sugar or glucose to the vat-liquor. Olphert adopts the use of steam, to raise the temperature of the vat to 111° F., and thus obtains 25 per cent. more colouring matter.

Japan possesses several large factories for preparing indigo from the native *Polygonum tinctorium*. The plants, 2–3 ft. high, are cut into three parts, the uppermost being the most valuable. The best dye is made from the leaves alone, which, after a few hours' exposure to air and sun, are placed in straw bags. They are afterwards removed from the bags and moistened with water, which must be proportioned with the greatest exactitude. They are then spread upon, and covered by, mats, for a few days, after which the sprinkling is repeated. The process continues for about 80 days, the moistening being renewed about 25 times for the best leaves,

and 9 for the inferior. After this fermentation, the leaves are pounded in wooden mortars for two consecutive days, by which they are reduced to a pulp; this is then formed into balls of dark-blue colour.

The central provinces of Java yield large quantities of indigo, which are exported to Holland, and thence widely distributed. The indigo prepared by the natives is of an indifferent quality, in a semi-fluid state, and contains much quicklime; but that prepared by Europeans is of a very superior quality. An inferior variety, having smaller seeds, and being of quicker growth, is usually planted as a second crop on land where one rice crop has been raised. In these situations, the plant rises to a height of about  $3\frac{1}{2}$  ft. It is then cut, and the cuttings are repeated three, or even four times, till the ground is again required for the annual rice crop. But the superior plant, when cultivated on a naturally rich soil, not impoverished by a previous heavy crop, attains a height of 5 ft., and grows with the greatest luxuriance. The plants intended for seed are raised in favourite spots, on the ridges of rice-fields in the neighbourhood of the villages, and the seed of one district is frequently exchanged for that of another. That of the rich mountainous districts, being esteemed of best quality, is occasionally introduced into the lowlands, and is thought necessary to prevent that degeneration which would be the consequence of cultivating for a long time the same plant upon the same soil. The climate, soil, and state of society of Java seem to offer peculiar advantages for the extensive cultivation of this plant. The periodical droughts and inundations of the Bengal provinces are unknown in Java, where the plant, in favoured situations, may be cultivated nearly throughout the whole year, and where it would be secure of a prolonged period of that kind of weather necessary for the cutting. The dye is prepared in a liquid state by the natives, by infusing the leaves with a quantity of lime; in this state, it forms by far the principal dye-stuff of the country. The indigos prepared in

Java by Sayers's process are of unusually high and constant quality. They contain an average of  $70\frac{1}{2}$  per cent. of indigotine, and a minimum of 65–66 per cent.; and an average of 2·77 per cent. of ash. Ordinary commercial indigos seldom attain 65–66 per cent. of indigotine; and their ash averages about  $16\frac{1}{2}$  per cent.

The Philippines produce considerable quantities of indigo, the best coming from Luzon. The plants suffer from locusts and storms, but the cultivation is very profitable. The yield of indigotine is large, but the preparation is conducted in such a primitive manner that the value of the product is much deteriorated.

In many parts of Africa, as Sierra Leone, Liberia, Abeokuta, the Niger valley, Natal, Cape Colony, Tunis, and the Soudan, species of indigo plants are found in a wild state, and from them the natives prepare an inferior dye-stuff.

In some of the S. States of America, notably S. Carolina, indigo culture has been attended with more or less success. The method of preparation pursued here varies but very slightly from the ordinary Indian process, almost the only important modification being the addition of a little oil to the liquor in the beating-vat, when the fermentation becomes too violent. The precipitated fecula is placed in coarse linen bags, and hung up to drain. The drying is finished by turning it out of the bags upon a floor of porous timber, and working it up. It is frequently exposed to the sun for short periods at morning and evening, and is then placed in boxes or frames, to cure till it is fit for the market.

Several of the Central American States have figured conspicuously as indigo producers. The dye is precipitated in the beating-vat by the sap contained in the bark of Tihuilate (*Yonidium*), Platanillo (*Myrosma Indica*), or Cuaja tinta. The fecula is left during the night; and, on the following day, is boiled, filtered, pressed, and sun-dried. In most districts, the cultivation is declining, partly owing to the carelessness exhibited in the preparation of the dye.

Indigo is judged commercially by its lightness, by a copper gloss on the surface, and by exhibiting no foreign ingredients when broken. There are several ways of testing it chemically, to ascertain the exact proportion of indigotine present; one method is as follows:—Finely pulverised indigo, 1 part; green copperas, 2 parts; and water containing 10 per cent. of caustic soda, 200 parts; are well boiled in a flask, and left to cool. The clear liquor is exposed in shallow vessels to the air, when the soluble indigo is oxidised, and precipitated as pure indigotine. The residue in the flask is thus treated three times; the whole indigotine is then collected on a filter, dried, and weighed. The consumption of indigo is still very large. Artificial indigo has not, as yet, been manufactured on a commercial scale, nor at a commercial price; but it has been produced, in the laboratory, from coal-tar derivatives, and further experiment may reveal a process for preparing the article at a sufficiently low price to compete with the natural colour.

Several preparations of indigo are in use:—(1) Sulphopurpuric acid, phenicine, or indigo-purple, is made by mixing 1 part of indigo with 4 parts of sulphuric acid (sp. gr. 1·845), and heating for  $\frac{1}{2}$ –1 hour; the acid mass is thrown into 40–50 parts of water, when the purple falls down; it is collected on a filter, and washed with dilute hydrochloric acid. (2) Sulphindigotic acid is prepared by mixing indigotine, 1 part, with sulphuric acid (sp. gr. 1·845) 6 parts; the operation must be performed in a leaden vessel, cooled outside, and the indigo must be added by degrees, to avoid heating; the mixture is then left for 8 days, when the conversion will be complete. Fuming or anhydrous acid may be used, in less proportion, but the reaction is more difficult to manage. Weaker acid will require a longer period, say a month for “brown acid” (145° Tw.). (3) Sulphindigotic acids are transformed into neutral paste, or “carmine,” by neutralising with carbonate of soda, and washing the paste, on a woollen filter, with a solution of chloride of sodium (common salt).

**Manganese Blue.**—(1) Kuhlmann found a blue mass of manganate of lime in furnaces used for making calcium chloride by calcining a mixture of chalk and residues from chlorine making. The formation of this beautiful coloured manganate he attributes to the decomposition of the calcium chloride by steam, and to a certain solubility of the lime in undecomposed calcium chloride. Unsuccessful attempts to reproduce this result were apparently due to the lime not being under such favourable conditions for acting upon the manganese oxide as when it is in solution in the calcium chloride. As accidentally produced in reverberatory furnaces, the manganate of lime is of an ultramarine tint, and is insoluble in water though not permanent under its influence; it is acted upon by the weakest acids.

(2) Bong has proposed several formulæ for making manganese blues, the ingredients in each case being heated to redness in an oxidising atmosphere, taking special care to avoid iron. The following are his recipes :—(a) 6 parts soda ash, 5 of calcium carbonate, 3 of silica, and 3 of manganese oxide; (b) 8 of barium nitrate, 2 of kaolin, and 3 of manganese oxide; (c) 8 of barium nitrate, 3 of silica, and 3 of manganese oxide. The tint can be varied from violet to green by altering the proportions.

**Prussian Blue.**—This blue owes its colour to a combination of iron and ferrocyanogen. The commercial products vary very much in tint, depth of colour, covering power, and solubility. They are used for a variety of purposes, nearly all of which require the blue to have some property different from what it should have for other uses. For some purposes a green shade blue is wanted, for others a violet shade blue; some users want the blue to be soluble in water, others for it to be soluble in oxalic acid, others require it to be insoluble. Ordinary Prussian blue is insoluble in water, acids, and alkaline salts; bleaching powder has no action on it, and therefore it is largely used for tinting paper. It is capable of resisting acids; but alkalis, such as caustic soda,

caustic potash, the carbonates of the same metals, lime and ammonia, decompose it, oxide of iron and a solution of a ferrocyanide of the alkali being formed, the decomposition being shown by a change of colour from blue to a reddish brown. On this account Prussian blues cannot be used for colouring soaps and alkaline products, or used as a pigment in distemper painting along with lime. The change of colour, from blue to brown, by the action of alkalies, distinguishes this blue from other blues.

Prussian blues require to be tested for their solubility in oxalic acid, by taking about 20 gr. of the blue, mixing with 1 oz. of water and 20 gr. of oxalic acid, in which a good blue ought to dissolve completely. Some brands are soluble in strong hydrochloric acid while others are not. It is decomposed by boiling sulphuric acid, and turned green by boiling nitric acid. For all the ordinary uses of a pigment Prussian blue is quite durable, and possesses a depth of colour and a definite tint which is proof against the destructive agencies of light and air; and though its covering powers are not great, it is one of the most important blue pigments in use.

When a salt of the higher oxide of iron is added to a solution of yellow prussiate of potash (or ferrocyanide of potassium) a blue compound is formed which is called Prussian blue. But this is not the method adopted for its commercial manufacture. In that case a ferrous salt, the proto-sulphate of iron, is added to a potassium ferrocyanide solution, the result of which is that a dirty bluish white precipitate is thrown down. On adding to this a little solution of bichromate of potash and sulphuric acid, the full deep blue is obtained. This is the industrial method of manufacturing Prussian blue.

*Yellow Prussiate.*—The first step is the preparation of the yellow prussiate of potash. The manufacture of this substance, although an industry of considerable importance, is comparatively little understood, either from a scientific or a

practical point of view. At all events, many prussiate makers seem completely at sea with regard to the most favourable conditions for carrying on the manufacture, and there can be no doubt that in many cases great waste occurs, through ignorance of the various reactions which take place during the process. The raw materials usually consist of carbonate of potash, iron filings or turnings, and organic matters containing carbon and nitrogen—such as dried blood, woollen rags, horn, hair, leather scraps, &c. The most suitable substances for use are, of course, those containing the largest proportion of nitrogen. The following are the percentages of nitrogen in various kinds of animal matter:—

Horn .. .. .. .. .. ..	15 to 17
Dried blood .. .. .. .. .. ..	15 to 17
Woollen rags .. .. .. .. .. ..	10 to 16
Sheep shearings .. .. .. .. .. ..	16 to 17
Calves' hair .. .. .. .. .. ..	15 to 17
Bristles .. .. .. .. .. ..	9 to 10
Feathers .. .. .. .. .. ..	16 to 17
Hide clippings .. .. .. .. .. ..	4 to 5
Old shoes .. .. .. .. .. ..	6 to 7
Horn charcoal .. .. .. .. .. ..	2 to 7
Rag charcoal .. .. .. .. .. ..	2 to 12

Animal matters always contain more carbon than is necessary for the formation of cyanogen by combining with the nitrogen also present. Consequently, when such substances are heated with pearlash, the excess of carbon reduces a portion of the carbonate to the metallic state, and this potassium combines with the cyanogen to produce potassium cyanide. The manufacture of yellow prussiate of potash may be conveniently divided into three stages: (1) The production of the molten mass technically known as "metal"; (2) the lixiviation; and (3) the crystallisation.

(1) The "metal" is made by fusing animal matters with pearlash, almost invariably with the addition of iron scrap. The animal substances are sometimes used in their original condition, whilst sometimes they are previously charred.

Generally speaking, however, a judicious mixture of the fresh and charred materials has been found to give the best results. The charcoal which is left on carbonising animal matters contains a certain amount of nitrogen, decreasing in proportion as the temperature rises ; but a smaller quantity of charcoal is also thereby produced. For example: 100 parts of rags carbonised at a certain temperature left 75 parts charcoal containing 12 per cent. of nitrogen, while the same rag carbonised at a higher temperature yielded 25 parts of charcoal, which contained only 2 per cent. of nitrogen. The animal matters employed should not leave much ash on ignition, as this would both thicken the mass and decompose a portion of the potash. In this respect sand is specially objectionable, for on ignition 1 part will decompose 2 of pearlash, owing to formation of silicate of potash. It is not necessary that the pearlash should be quite pure ; in fact, a certain proportion of sulphate is stated to be useful, as it is changed into sulphide by ignition with the carbonaceous materials.

The theory of the formation of yellow prussiate of potash may be briefly stated as follows : The carbonate and sulphate of potash react with the carbon, nitrogen, and iron, forming in the first instance sulphide of potassium, which afterwards converts the iron into sulphide, whilst potassium cyanide is simultaneously produced. It should be here explained that ferrocyanide of potassium (yellow prussiate) is not formed during the ignition of the above mentioned materials, but results from the lixiviation of the fused mass with water, when the cyanide of potassium and iron sulphide decompose each other, producing ferrocyanide and sulphide of potassium. It is quite obvious that even if any ferrocyanide were produced during the process of fusion, it would almost immediately be decomposed, at the intense heat to which the mass is subjected, into potassium cyanide, iron carbide, and nitrogen gas. If any doubt were felt on this point, the experiments of Liebig conclusively prove that the formation

of ferrocyanide takes place on dissolving the ignited mass in water, but not previously. Liebig found that if the fused mixture be allowed to cool, and then treated with moderately strong alcohol, potassium cyanide alone is extracted, and the residue when dissolved in water no longer yields ferrocyanide. As ferrocyanide is not formed during the process of fusion, the presence of iron in the preliminary stages may appear superfluous ; but such is not the case. The presence of iron is necessary for two reasons, firstly, because the sulphate of potash which is generally present is converted into sulphide and bisulphide, and these, in the absence of iron, would decompose some of the cyanide of potash into sulphocyanate, thereby causing a loss of cyanogen so far as yellow prussiate is concerned ; and secondly, because potassium bisulphide has a very corrosive action on the iron pot in which the fusion takes place. When iron is present it readily decomposes any alkaline sulphides, thereby preventing formation of sulphocyanate, and being itself converted into iron sulphide, which is again changed into prussiate by the action of the aqueous cyanide.

Pear-shaped iron pots were formerly used for fusing the raw materials. The arrangement now generally adopted in large English works consists of a series of iron pots almost hemispherical in shape, set in brickwork, and each heated by a separate fire and circular flue. These vessels are closed by iron lids, with apertures for the admittance of animal matters, the aperture being at once closed by a slide after each addition. Through every lid there passes a vertical spindle, carrying a set of blades for mixing the materials, and set in motion by a suitable shaft worked by steam power. Instead of the ordinary iron pots, reverberatory furnaces are often employed, especially in Germany. The reason for this preference is, that ordinary iron vessels are worn out in a comparatively short time, the destructive action being greatest on the under surface of the muffle. A much larger quantity of raw material can also be operated

upon at one time if a reverberatory furnace be used. The mode of procedure depends to some extent upon the condition of the organic materials employed. If fresh, the muffle or furnace must be left open, so as to permit the mixture to be well and frequently stirred, and additions to be made at intervals until eventually ammonia ceases to be evolved. The furnaces are arranged in such a manner that when the carbonate of potash has once become fused the doors of the fire-place may be shut, and no fresh firing is required during the introduction of the animal matters. The molten mass is kept well stirred by means of a thick iron bar, suspended by a chain, and fixed in an aperture in the side of the furnace. By the use of this arrangement the stirring is much more easily and thoroughly effected than is the case with the old fashioned pots. Ordinary reverberatory furnaces cannot be used for the fusion, because the silica in the hearth would combine with the potash to form silicate of potash. Gas generators with air blast are now sometimes employed instead of ordinary fuel in the manufacture of yellow prussiate of potash. Several advantages are gained by operating in this manner, especially that of permitting the regulation of temperature and the admission of oxygen, so as to obtain an ordinary, a neutral, or a reducing flame, according to requirements. In the preparation of the "metal," for every 100 parts of pearlash from 100 to 125 parts of fresh animal substances are required, together with 6 or 8 parts of iron in some form or other. The pearlash, or a mixture of 1 part of pearlash with 2 to 4 parts "blue salt" or "blue potash" (this substance will be referred to later on), is melted in the furnace and heated to bright redness, so that the temperature of the mass may not be reduced too much by the addition of the animal matters. These, in their original condition, or an equivalent quantity of carbonised materials, together with the proper proportion of iron, are then introduced—first pretty frequently, afterwards at longer intervals. Each addition of animal matter causes a somewhat violent frothing and escape of combustible

gases, along with water and carboric acid, and the whole becomes thick—not so much owing to the introduction of solid substances as by the fall of temperature, resulting from the production of such large quantities of gas. In order to hasten the decomposition, vigorous stirring must be applied. When the reaction is at an end, the semi-fluid mass is transferred to cast-iron dishes, and the furnace is again filled with carbonate of potash and heated. In this way four or five charges may be accomplished every day, and the process carried on continuously. The most favourable conditions for effecting the melting part of the process are attained when the heat approaches whiteness, and a bright, clear flame is produced as soon as the raw materials are introduced. According to one authority, woollen rags and good pearlash, with a small proportion of waste iron, have produced the largest yield of yellow prussiate, although even in this case two-thirds of the total nitrogen present was lost in the form of ammonia.

(2) Lixiviation.—The fused mass, if properly prepared, should yield about 16 per cent. of prussiate on dissolving in water. In this part of the process, the “metal” when cold is broken into lumps and placed in cold water mixed with the weak lyes from former operations. Heat is then applied until the temperature rises to about  $180^{\circ}$ – $190^{\circ}$  F., and the liquid is stirred vigorously so as to promote rapid solution, because some of the potassium cyanide is apt to be decomposed during lixiviation. When the solution attains a density of  $30^{\circ}$ – $40^{\circ}$  Tw. it is left to clarify, the heat being withdrawn. The clear solution is decanted, and evaporated in pans, which are generally heated by the waste heat of the furnaces. When it has a density of  $54^{\circ}$  Tw. it is run off into the crystallisers, where it deposits the crude salt.

(3) Crystallisation.—This is a very important stage of the manufacture, as it is the final process by which the crude prussiate is rendered sufficiently pure to be placed on the market. The impure substance is dissolved in warm water until the solution stands at  $54^{\circ}$  Tw.; after all in-

soluble matter has deposited, the clear liquor is placed in the crystallising vessels. These are occasionally made of wood; but when such vessels are used, the crystallised salt generally possesses a green colour, which is believed to be due to the tannin present in the wood. On this account cast-iron crystallisers are more frequently employed. The crystallisation proceeds slowly—often going on for several weeks in large vessels. The mother liquor is then drawn off, and if not too impure is used for dissolving fresh quantities of the crude prussiate. The ferrocyanide is deposited in crusts in the crystallisers; but by hanging lumps of the solid salt in the solution, long clusters of crystals may be obtained, and by suspending these in fresh prussiate lyes immense crystals are produced. From 100 parts crude prussiate about 90 parts pure potassium ferrocyanide are obtained, or sometimes in the case of purer materials 97 parts.

Sulphate of potash is often present in commercial yellow prussiate. The separation of this impurity is best effected on the large scale by evaporating the prussiate solution to a density of 62° Tw., at which point most of the sulphate will crystallise out. If the clear liquor be then drawn off, diluted to 52° Tw., and allowed to cool, almost pure potassium ferrocyanide will gradually deposit. This may be rendered absolutely pure by gently fusing the crystals, dissolving in water, and treating with a small quantity of acetic acid, which will decompose any carbonates and cyanides. On adding sufficient strong alcohol, the ferrocyanide is precipitated, and when crystallised once or twice more from water it may be regarded as chemically pure.

Blue salt.—This substance, to which we have previously referred, is a residue obtained in the manufacture of prussiate of potash. The last mother-liquor contains a large quantity of carbonate of potash, along with smaller amounts of hydrate, silicate, chloride, and sulphocyanate. It is concentrated until the liquid has a density of 90° Tw., when most of the chloride, silicate, &c., separates out, and the strong liquor

containing the greater proportion of the carbonate is evaporated to dryness, and calcined in a reverberatory furnace. The dry residue constitutes the "blue salt" or "blue potash," and contains from 70 to 80 per cent. carbonate of potash. It may be employed instead of pearlash, or mixed with it, for the next batch of yellow prussiate. The composition and amount of the insoluble residue left on lixiviation of the "metal" vary according to the proportions and character of the raw materials used. Other conditions being equal, horn gives the lowest percentage of insoluble matter on lixiviation.

The large proportions of potash and phosphates contained in the insoluble residues render them well suited for use in the manufacture of artificial manures. As already mentioned, when regarded from a scientific or economical point of view, the yellow prussiate industry is carried on under very imperfect conditions. In addition to the amount of potash, there is a very considerable waste of nitrogen, firstly, because the larger proportion of that element present in the animal substances is not converted into cyanogen at all, but passes off chiefly in the form of ammonia salts; and, secondly, because part of the potassium cyanide which is actually produced is lost by decomposition, and another portion is left in the mother liquor. It has been calculated that out of every 100 parts of ferrocyanide which should theoretically be obtained, 4 parts are lost when fairly pure materials have been employed, and 14 in the case of impure ingredients.

The following analyses indicate the percentage composition of two samples of insoluble residue:—

	No. 1.	No. 2.
Sulphate of potash, &c. .. .. .. ..	9·06	3·21
Phosphates of lime, magnesia and iron .. ..	13·74	6·24
Oxide of iron .. .. .. ..	13·34	19·58
Lime and magnesia .. .. .. ..	5·08	7·23
Sand and silica .. .. .. ..	23·97	29·24
Charcoal and moisture .. .. .. ..	34·81	34·50
	100·00	100·00

According to Karmrodt, the following proportions of the nitrogen contained in various animal substances are actually converted into cyanogen during the manufacture of yellow prussiate of potash :—

	Per cent.
Woollen rags .. .. .. .. .. .. .. ..	16
Horn .. .. .. .. .. .. .. ..	20
Leather cuttings .. .. .. .. .. .. .. ..	33
Cow hair .. .. .. .. .. .. .. ..	14
Dried blood .. .. .. .. .. .. .. ..	16
Horn charcoal .. .. .. .. .. .. .. ..	56
Rag charcoal .. .. .. .. .. .. .. ..	33

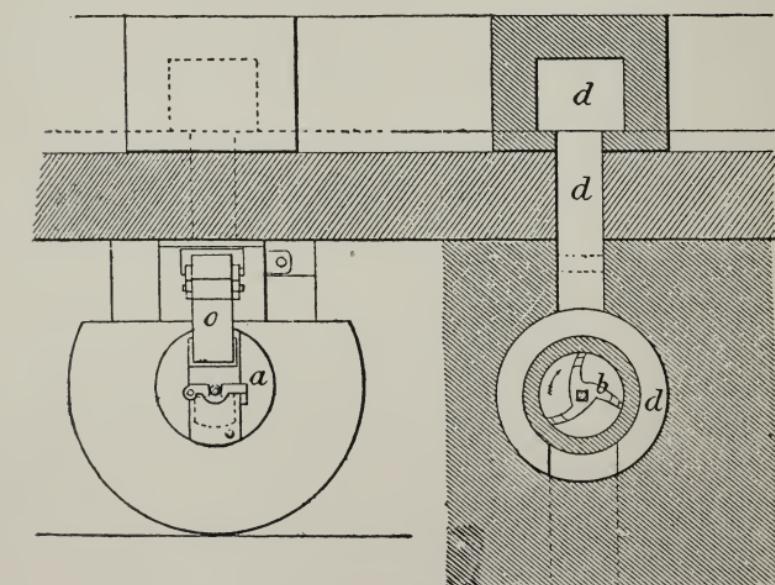
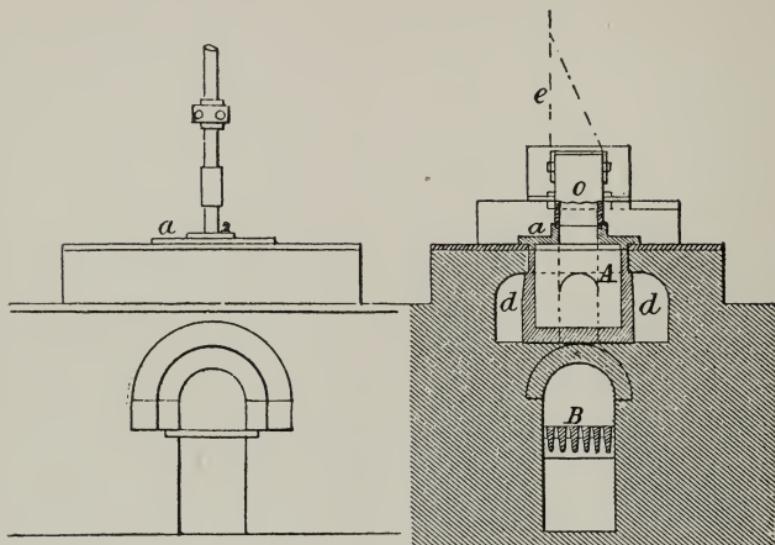
As is well known, human excreta contain a considerable proportion of nitrogen, and there seems no reason why this should not be employed in the manufacture of yellow prussiate. It is quite possible that municipal bodies might find this a convenient and profitable plan of disposing of a portion of the sewage with which they have to deal. It is obvious to all persons who have given this subject much consideration, that the nitrogen required in the manufacture of yellow prussiate of potash might be obtained with comparative ease from the surrounding atmosphere. Indeed, from a theoretical point of view this seems a charming process. About fifty years ago the Society of Arts awarded Lewis Thompson a medal in connection with this very process. Thompson ignited a mixture of 2 parts pearlash, 2 parts coke, and 1 part iron turnings in an open crucible for a considerable time at a full red heat. The resulting black mass was found to contain a large quantity of ferrocyanide, together with excess of carbonate of potash, &c. This process, or a similar one, in which a current of air was passed over a mixture of charcoal and iron saturated with carbonate of potash, was tried on a large scale for two years at Bramwell's works at Newcastle. About 1 ton of yellow prussiate was made daily by this process; but it was not found to work profitably, and was eventually abandoned, chiefly, it is said, owing to the large

amount of fuel required, and because the cylinders, whether of iron or fireclay, were not able to stand for any length of time the intense heat to which they were subjected.

The annexed illustrations, Figs. 14 to 17, show the arrangement of a prussiate of potash furnace at Sir E. Buckley's works, at Clayton, Manchester, which are well designed to prevent nuisance : A, iron pot ; B, fire-place ; *a*, cover of pot ; *b*, stirrer ; *c*, hinged pipe conveying vapours to the flues ; *d*, flues surrounding the pot, and leading to the chimney-shaft ; *e*, chain to lift up cast-iron vapour hood.

Brunquell, a German manufacturer, has criticised the present method of conducting operations, and proposes that it is necessary as far as practicable to aid the secondary formation of cyanogen by ammonia and incandescent charcoal, and to avoid loss of potash by using pure animal substances, and preventing contact with the solid products of combustion from the furnace. With this view he adopts a horizontal reverberatory furnace, the hearth of which is a cast-iron tray about  $4\frac{1}{2}$  ft. long, 4 ft. wide, and  $3\frac{1}{2}$  in. deep. The crown of the furnace is built as flat as possible, the working space is limited, and the charge is kept from contamination by the fire. Such a furnace, despite certain drawbacks, presents important advantages. Fuel is economised ; the process is hastened so that seven or eight charges can be dealt with in a day, instead of only four ; and the furnaces cost less and endure longer. The charge consists of 220 lb. potash, of which two-thirds is from evaporated mother-liquors, and one-third fresh ; 44 lb. animal charcoal from the carbonisation of substances poor in nitrogen ; 140–150 lb. of pure animal matters as dry as practicable ; and  $17\frac{1}{2}$  lb. iron. The firing is urged and the charge is stirred till all the potash is fused, when the ash-pit is closed, and the damper turned on for charging half the animal charcoal. The firing and stirring are again pushed on till the proper consistency is attained, and potassium vapour begins to burn off. In this state the mass is ready to receive the animal

substances, those rich in nitrogen being first added in small portions at a time. Their effect is to render the mass hard,



Figs. 14, 15, 16, 17.—YELLOW PRUSSIATE FURNACE.

dry, and difficult of fusion, whereupon the remainder of the animal charcoal should be promptly introduced. After thorough agitation, the working door is closed for a short time, and the contents of the furnace are rapidly discharged into a covered iron pan.

The character of the animal matters employed varies so much that it is impossible to lay down hard and fast rules for the proportions of the several ingredients, or the duration of the roasting. Nor is the value of a raw material always in proportion to its richness in nitrogen, because the poorer material may waste less potash, consume less fuel, and require less labour. The addition of iron filings or turnings is useful only in prolonging the life of the cast-iron crucibles.

*Combination of the Cyanide and Iron Solutions.*—A great number of recipes are in vogue for combining the two solutions of ferrocyanide and an iron salt, both with reference to their proportions, and to the addition of foreign matters of various kinds. These variations in the formulæ give rise to distinct names for some kinds of Prussian blue, which will be referred to below. The ordinary common Prussian blue has a greenish tendency, and is chiefly made according to one or the other of the following directions :—

(1) Mix a solution of 100 lb. yellow prussiate with a solution of 100 lb. green copperas (ferrous sulphate) and 18 lb. alum, to which 9 lb. sulphuric acid has been added, and let the mixture stand for 2–3 hours, or until the solid portion has completely settled out. Decant the clear supernatant liquor, and well wash the precipitate with clean waters. Finally throw it on a filter and subject it to repeated disturbance, so as to ensure the admission of air to every particle, in order that the requisite oxidation may take place. The proportion of alum used is subject to very great variation according to individual fancy ; it renders the subsequent grinding of the pigment a very much easier matter,

but it causes the shade of blue to be paler than it otherwise would be.

(2) The simple solutions of green copperas and yellow prussiate in equal proportions are mixed together without any other ingredient being added, and the precipitate produced is washed, filtered, and aërated as in (1). It is, however, inferior by reason of the oxide of iron formed in the pigment spoiling the purity of the colour, and necessitating the treatment of the wet mass with hydrochloric acid, at some expense, for removal of the iron oxide.

ANTWERP BLUE.—This pale variety of Prussian blue has but little importance now. It is prepared by adding a solution of 4 lb. yellow prussiate in 5–6 gallons of water to one of 2 lb. sulphate of iron, and 1 lb. each of alum and sulphate of zinc in an equal quantity of water. The resulting pigment consists of a mixture of the ferrocyanides of iron, alumina, and zinc; it is washed, filtered, aërated, and dried as other forms of Prussian blue.

BONG'S BLUE.—When cyanide of potassium is added to an acid solution of a copper salt, a red colour is produced, which has already been mentioned by different observers. The substance formed is very changeable, at least in the liquid where it is formed. It is decomposed by acids, alkalies, cyanide of potassium, and even decomposes spontaneously, the colour changing to yellow. It is precipitated by insoluble cyanides; hence when a dilute acid is added to the red solution, the dye is at once thrown down along with the cyanide of copper. If the precipitate thus obtained is treated with sulphuretted hydrogen, it is decomposed and the substance is set free. This substance can combine with iron, like cyanogen, so as to conceal the properties of the iron. This compound is very permanent, and has lately been studied by Bong, who gives the following directions for its preparation:—

Cyanide of potassium is added in excess to an acid solution of a copper salt until the red colour at first formed has

disappeared, when a ferric salt is at once added. On the addition of the iron salt, of course, a copious precipitation of Prussian blue takes place, and the liquid again turns to a dark purple-red. To separate the colouring substance from the alkaline salts in the liquid, a dilute acid is added, which precipitates it and the cyanide of copper. This precipitate is combined with the Prussian blue, which also contains a considerable quantity of the colouring substance, and then treated with a boiling solution of carbonate of ammonia, in which it dissolves. As the cyanide of copper also goes into solution, it is separated by again precipitating it with an acid, and treating the precipitate with sulphuretted hydrogen. The colouring substance thus liberated now contains a certain amount of hydroferrocyanic acid, which is removed after neutralisation by acetate of lead. It is now filtered, and the purification is completed by precipitating with a silver salt and treating the precipitate with sulphuretted hydrogen.

This purple-coloured compound crystallises very indistinctly. To determine its composition, Bong precipitated it with acetate of copper. When dried at 212° F., the rose-coloured precipitate had the following composition: Carbon 24·31, nitrogen 28·04, hydrogen 1·88, iron 13·66, copper 17·67, oxygen 14·44. Total 100·00. These numbers correspond to the formula  $Cu, Fe Cy_4 (HO)_4$ .

This substance is likewise precipitated by salts of zinc, mercury, and silver. All these precipitates are pink or purple, very beautiful, and of remarkable brilliancy. They are soluble in alkalies. Iron salts yield no precipitate, nor do lead salts, except in the presence of ammonia, when a blue-violet precipitate is formed. When treated with sulphuretted hydrogen, these precipitates yield purple-red and acid liquids, which undergo change in the air, especially if warm, forming Prussian blue. When these liquids are neutralised with alkali, purple compounds are formed, which are permanent in the air, soluble in water, slightly so in alcohol, and insoluble in ether. Their colouring power is

exceptionally great. These pigments will unite with ferrocyanides, and in its preparation such a compound is produced in considerable quantity; it is likewise of a purple colour, and gives a rose-coloured precipitate with acetate of lead. Both alone and in this compound it is very permanent; it resists the action of sulphurous acid, concentrated and boiling alkalies, and dilute acids, but is rapidly destroyed by chlorine and nitric acid. If this pigment could be prepared cheaply enough, it would probably be used with advantage in the arts, on account of its resistance to chemical reagents and light, the variety of its shades, and its brilliancy. It does not colour fibres directly, but can readily be fixed on them from slightly acid solutions, if they are previously mordanted with metallic oxides.

BRUNSWICK BLUE.—This pigment is made in pale, medium, and deep shades, and is an extremely useful colour, being very fine, requiring no grinding, thoroughly permanent in light and air, hardly acted upon by acids, but turned brown by alkalies, and liable on standing to separate into two portions—a white and a blue—the latter coming to the surface while the former sinks, and necessitating a thorough stirring of the paint before use.

It generally consists simply of barytes, or gypsum, or china clay, coloured by a small percentage of Prussian blue, with or without the addition of a lesser proportion of ultramarine. The barytes or other base is very thoroughly agitated in water, while a solution of green copperas and a solution of yellow prussiate are gradually added without ceasing the agitation. When the incorporation of the ingredients has been completely accomplished, the precipitate is settled, washed, filtered, and dried. Following are a few recipes:—

- Pale. (1) 1 cwt. barytes, 1 lb. green copperas, 1 lb. yellow prussiate.
- Pale. (2) 1 cwt. china clay, 2 lb. green copperas, 2 lb. yellow prussiate.
- Pale. (3) 1 cwt. gypsum, 1½ lb. green copperas, 1½ lb. yellow prussiate.

Medium. (1) 1 cwt. barytes, 3 lb. green copperas, 3 lb. yellow prussiate.

Medium. (2) 1 cwt. china clay, 6 lb. green copperas, 6 lb. yellow prussiate.

Medium. (3) 1 cwt. gypsum,  $4\frac{1}{2}$  lb. green copperas,  $4\frac{1}{2}$  lb. yellow prussiate.

Deep. (1) 1 cwt. barytes, 5 lb. green copperas, 5 lb. yellow prussiate.

Deep. (2) 1 cwt. china clay, 10 lb. green copperas, 10 lb. yellow prussiate.

Deep. (3) 1 cwt. gypsum,  $7\frac{1}{2}$  lb. green copperas,  $7\frac{1}{2}$  lb. yellow prussiate.

In each case about 50-60 gallons of water are required.

To determine the amount of barytes present in a sample, boil about 50 gr. with caustic soda, filter, wash the residue free from soda, treat with sulphuric acid, well wash the insoluble residue, dry, and weigh.

**CHINESE BLUE.**—This well-known and favourite form of Prussian blue is prepared with great care, and is usually sold in fine powder or little cubes. Its composition is virtually identical with that of ordinary Prussian blue, but it is more free from impurities, and shows a fine bronze bloom or lustre on newly fractured surfaces. Being pure, it is entirely dissolved by oxalic acid; and its composition is about 52 per cent. oxide of iron,  $43\frac{1}{2}$  cyanogen, and  $4\frac{1}{2}$  water. In dyeing and calico-printing it is extensively employed. Its tint varies from greenish to violet, according to modifications in the method of manufacture, the chief difference being that yellow prussiate gives a greenish tone and red prussiate a violet.

The process of preparation is mainly as follows. In about 40 gallons of cold water dissolve 1 cwt. of green copperas selecting it carefully for freedom from insoluble oxide; add about 5 pints of sulphuric acid. This liquor very rapidly undergoes oxidation, by which oxide of iron is thrown down, and the solution is rendered unfit for making the best quality pigment. Therefore it should be prepared only immediately before it is used. In another vessel containing

about 40 gallons of cold water, dissolve 1 cwt. of yellow prussiate (if a green shade is desired), or of red prussiate (if a violet tint is wished for). Even larger quantities of water may be used for the solutions, as the more dilute they are the finer is the colour precipitated and the greater the lustre on the surface of the finished pigment.

When the two solutions of yellow or red prussiate and acidified green copperas are brought together, a bluish-white precipitate is thrown down. This is allowed to completely separate itself, and then the clear supernatant liquid is drawn off.

The next step is to thoroughly oxidise the precipitate. This cannot be satisfactorily accomplished by utilising the oxygen of the atmosphere, as is done in other cases, because that method entails the production of a certain amount of oxide of iron, which prejudicially affects the purity of colour of the finished article. Of the chemical oxidising agents which are available, the most satisfactory in point of cost and efficiency is chloride of lime (bleaching powder). For each cwt. of green copperas, mix about 20 lb. of bleaching powder into a thin cream with water, and add it, in small quantities at a time, to the precipitate, constantly stirring so as to ensure the absorption of the whole of the chlorine by the blue. Without the addition be made gradually and under agitation, the chlorine will be generated more quickly than it can be absorbed, entailing a waste of gas and a noxious vapour to be breathed by the workmen. Sometimes the bleaching powder is added at an earlier stage, viz. to the green copperas solution, and in that case the blue assumes a violet tone.

After the addition of the bleaching powder solution to the bluish-white precipitate, it is acidified with hydrochloric acid, which develops the blue. When the whole has settled, the supernatant liquor is drawn off, and the blue powder is well washed and strained on a filter, then placed in pans and dried very gradually indeed in the dark, at a tempera-

ture never exceeding 130° F. The slower the drying the better is the gloss of the pigment. It is most essential that iron be excluded during the final grinding operation, or it may cause ignition of the mass, and its conversion into oxide of iron would speedily follow.

It has been proposed to treat the white precipitate (obtained in the usual manner from green copperas and yellow prussiate) by the chlorine contained in aqua regia (nitro-hydrochloric acid). The copperas, however, must be as free as possible from basic sulphate (oxide), which is ensured by keeping a little metallic iron in the acid solution of copperas. It is also desirable to effect the precipitation with crude prussiate, so as to avoid absorption of oxygen and premature development of the blue colour. Habich considers that the mistake is generally made of using too little copperas, and he has found that when 90 lb. of copperas have been added to 100 lb. of yellow prussiate, a drop of iron solution in the filtered liquor produces no precipitate, while the white precipitate has carried with it a certain proportion of prussiate, which can be washed out. He therefore proposes to avoid this waste by pouring the copperas solution into the prussiate solution, with constant agitation, till no further precipitate goes down, then adding one volume of the copperas solution equal to one-ninth of that already used. After fifteen minutes stirring, it is certain that all the prussiate carried down is decomposed.

The drained precipitate is blued (peroxidised) by adding aqua regia prepared several days previously, and in proportions depending on the strengths of the two acids. Generally, the aqua regia mixture will be 100 lb. of commercial nitric acid at 30° B. (containing 35·4 lb. of anhydrous acid) and 62·2 lb. commercial hydrochloric acid at 23° B. (containing 23·9 lb. of the anhydrous acid); and 40 lb. of this mixture will suffice for bluing the precipitate resulting from 100 lb. yellow prussiate. The addition of

the aqua regia should take place in a wooden vessel with constant agitation.

According to another modification, the white precipitate obtained in the usual way is blued by adding a solution of perchloride of iron, which may be made from a hematite ore free from clay and carbonate of lime, or from rouge. The iron oxide, from whatever source, is ground to a very fine state, and treated with crude hydrochloric acid in a lead-lined tank, where the mixture remains for several days, and is constantly stirred. When saturated with iron the clear liquid is withdrawn for use. To receive it, the white precipitate is rapidly heated to boiling in a copper vessel, and is then transferred to a wooden vat, and the iron perchloride solution is stirred in till the desired tint is produced. The pigment is washed and dried in the ordinary way, while the supernatant liquor (essentially protochloride of iron) is poured over old scrap iron and used instead of copperas for a fresh batch of yellow prussiate.

A solution of perchloride of manganese may be used instead of perchloride of iron. Inferior qualities of manganese ore can be employed, and the residues left after treatment with hydrochloric acid may be washed and dried for sale as purified or peroxidised manganese.

PARIS BLUE.—(1) A synonym for the violet-tinted kind of Prussian blue.

(2) A series of compounds described below. [a] A thorough mixture of 2 parts sulphur and 1 part dry carbonate of soda is gradually heated in a covered crucible to redness or till fused; a mixture of silicate of soda and aluminate of soda is then sprinkled in, and the heat is continued for an hour; the little free sulphur present may be washed out by water. [b] An intimate mixture of 37 parts china-clay, 15 parts sulphate of soda, 22 parts carbonate of soda, 18 parts sulphur, and 8 parts charcoal, is heated in large crucibles for 24–30 hours; the mass is re-heated in cast-iron boxes at a moderate temperature till the desired

tint appears, and is finally pulverised, washed, and dried. [c] Gently fuse 1075 oz. crystallised carbonate of soda in its water of crystallisation; shake in 5 oz. finely-pulverised orpinent, and, when partly decomposed, as much gelatinous alumina hydrate as contains 7 oz. anhydrous alumina; add 100 oz. finely-sifted clay, and 221 oz. flowers of sulphur; place the whole in a covered crucible, and heat gently till the water is driven off, then to redness, so that the ingredients sinter together without fusing; the mass is then cooled, finely pulverised, suspended in river-water, and filtered. The product is heated in a covered dish to dull redness for 1-2 hours, with occasional stirring. Colourless or brownish patches may occur, and must be removed.

SAXON BLUE.—Following is a recipe for the preparation of this pigment, which possesses limited importance.

Dissolve 8 lb. alum and 1 lb. green copperas in 16 gallons of water. Add separate solutions of pearlash and yellow prussiate till precipitate ceases to go down. Collect the precipitate when it has completely settled; wash thoroughly, and dry.

SOLUBLE BLUE.—This term is applied to a variety of Prussian blue which, while possessing no difference in the matter of chemical composition, yet has the distinctive feature of being soluble in water, which the other varieties are not. It no longer enjoys the popularity it once had as a dye, on account of the severe competition of the coal-tar colours. Below are some of the most satisfactory formulæ for its preparation.

(1) Mix 10 lb. of Prussian blue thoroughly in about 10 gallons of cold water. Then add 5 lb. of yellow prussiate and let the whole mass boil steadily for several hours. Strain off the liquor and well wash the precipitate on a filter. Finally dry for use.

(2) Dissolve about 1 cwt. of red prussiate in water and make the solution hot. Prepare another solution of about 73 lb. of green copperas in hot water. Mix the two solutions together and boil them for about a couple of hours. Allow the

solid matters to settle out, then put them on a filter and wash with clean water until a blue coloration manifests itself in the drainings. The blue residue is then dried as usual.

(3) Make one solution of 10 lb. of yellow prussiate, and another of 8 lb. of green copperas, water being the solvent in both cases. Mix these two solutions together and give them an hour's boiling.

Add 3 lb. of a mixture of nitro-sulphuric acid, containing 2 parts of the former to 1 of the latter. Boil for another hour. Let the solid pigment precipitate itself thoroughly, and then filter, wash, and dry as in the other cases.

(4) Dissolve about 1 cwt. of perchloride of iron and 10 lb. of sulphate of soda in water. Also dissolve in another vessel 2 cwt. of yellow prussiate and 10 lb. of sulphate of soda. Pour the first solution into the second (never the contrary) and take care that the prussiate solution is always preponderant. The Glauber's salt is useful in rendering the precipitation of the blue pigment more complete by reason of the insolubility of the latter in saline fluids. When the blue sediment is all thrown down it is drained off on a filter, and repeatedly washed till a blue tint appears in the wash-waters, when it is dried for use.

TURNBULL'S BLUE.—This is an old-fashioned name often applied, like the term Paris blue, to the violet shades of Prussian blue which have been prepared with red prussiate.

Ultramarine.—According to Rowland Williams, F.C.S., natural ultramarine is, perhaps, the most beautiful blue pigment known. It was formerly, and is now to a small extent, manufactured (chiefly for artists' use) from lapis lazuli, a blue mineral which occurs, intermixed with limestone and iron pyrites, in Siberia, Thibet, and China. In order to obtain ultramarine from lapis lazuli, the roughly pulverised mineral is ignited, dipped into vinegar to remove carbonate of lime, and then reduced to the finest possible

state of division. The powder is next mixed with a cement composed of rosin, linseed oil, white wax, and Burgundy pitch, and the resultant paste is worked under water until all the ultramarine is separated. The ultramarine is washed several times with water, and afterwards with alcohol, which removes any of the resinous compound which may have adhered. When treated in this manner, lapis lazuli yields from 2 to 3 per cent of ultramarine. According to Clement and Desormes, lapis lazuli has the following composition:—

	Per cent.
Soda .. .. .. .. .. .. .. ..	23·2
Alumina .. .. .. .. .. .. .. ..	34·8
Silica .. .. .. .. .. .. .. ..	35·8
Sulphur .. .. .. .. .. .. .. ..	3·1
Carbonate of lime .. .. .. .. .. .. .. ..	3·1
<hr/>	
	100·0

It will be seen, therefore, that ultramarine essentially consists of alumina, silica, soda, and sulphur, and may be regarded as a sodium aluminium sulphate, in combination either with polysulphide of sodium alone, or with a polysulphide and a polythionate of sodium. Clement and Desormes believe that the iron in lazulite (lapis lazuli) is an accidental impurity, and is neither essential to the mineral itself nor to the ultramarine derived from it. There is still some doubt on this point, however, many eminent chemists holding the opinion that iron is a necessary constituent of ultramarine blue.

Natural ultramarine has been almost entirely replaced by the artificial product, since methods have been devised for the manufacture of the latter on a large scale. The possibility of preparing artificial ultramarine suggested itself in a curious manner. About seventy years ago a French alkali maker noticed the occasional appearance of a blue coloured substance in his soda furnace. On analysis, Vauquelin found the substance to have the same chemical compo-

sition as lapis lazuli, and this incident led him to believe that ultramarine might be built up from its elements. Several years passed away before Guimet succeeded in manufacturing artificial ultramarine on anything like a large scale, but Gmelin is said to have prepared it in small quantity half a dozen years previously. There are four varieties of artificial ultramarine: (1) the pure deep blue, equal in colour to average native ultramarine; (2) pale blue; (3) violet or pink ultramarine; (4) green ultramarine. The latter is obtained in the first stage of the ultramarine manufacture, being the result of incomplete ignition of the materials employed. Ultramarine is generally manufactured by one of the following processes:—(a) “Sulphate”; (b) “Soda”; (c) “Silica.”

(a) “Sulphate” Ultramarine.—This may be prepared from sulphate of soda (Glauber’s salt), charcoal, and kaolin (china clay). The materials should be as free as possible from iron, and it has been found that clay having approximately the formula  $\text{Al}_2\text{O}_2(\text{SiO}_2)_2$  gives the best results. The clay and sulphate of soda must be thoroughly calcined. They are then intimately mixed with charcoal in the following proportions:—

	Per cent.
Clay .. .. .. .. .. .. .. .. ..	48·3
Sulphate of soda .. .. .. .. .. .. .. ..	43·5
Charcoal .. .. .. .. .. .. .. .. ..	8·2
	<hr/>
	100·0

Sometimes a portion of the sulphate of soda is omitted, and some carbonate of soda and sulphur added instead. The composition of the mixture then becomes:—

	Per cent.
Clay .. .. .. .. .. .. .. .. ..	47·2
Sulphate of soda .. .. .. .. .. .. .. ..	19·3
Carbonate of soda .. .. .. .. .. .. .. ..	19·3
Charcoal .. .. .. .. .. .. .. .. ..	8·1
Sulphur .. .. .. .. .. .. .. .. ..	6·1
	<hr/>
	100·0

Caustic soda is also sometimes used instead of carbonate. These mixtures (whether sulphate alone or sulphate and carbonate) are made with a view to have the soda present in sufficient amount to combine with one-half the silica contained in the clay, and to leave sufficient soda to form polysulphide of sodium with a portion of the sulphur. There should then remain enough soda and sulphur to produce ordinary sulphide of sodium ( $\text{Na}_2\text{S}$ ). If either of the two mixtures be ignited out of contact with air, a white compound is formed, which is sometimes termed white ultramarine. On leaving this exposed to the atmosphere for some time it becomes green, and on further ignition, with free access of air, it is converted into ultramarine blue. In actual working the carefully prepared mixture of the above mentioned materials is heated for several hours to a high temperature in fire-clay crucibles, only a limited supply of air being allowed to enter, and the temperature being eventually raised to a white heat. The product of this operation, when cool, has a grey or yellowish-green appearance. It is washed several times with water, dried, reduced to a fine powder, and then represents the green ultramarine of commerce. Stölzel found that green ultramarine had the following composition :—

	Per cent.
Alumina .. .. .. .. .. .. .. ..	30·11
Silica .. .. .. .. .. .. .. ..	37·46
Sodium .. .. .. .. .. .. .. ..	19·09
Sulphur .. .. .. .. .. .. .. ..	6·08
Iron .. .. .. .. .. .. .. ..	·49
Calcium .. .. .. .. .. .. .. ..	·45
Chlorine .. .. .. .. .. .. .. ..	·37
Oxygen .. .. .. .. .. .. .. ..	5·19
Sulphuric acid .. .. .. .. .. .. ..	·76
Magnesia, potash, and phosphoric acid ..	traces.
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	100·00

Green ultramarine is transformed into blue by heating with about 4 per cent. of sulphur at a low temperature, with free

access of air. Sulphur is afterwards added, if necessary, in small quantities at a time, and the heating is continued until the desired shade of blue is obtained. The mass is then powdered, the soluble matter (sulphide of soda, &c.) is removed by washing with water, and the blue is dried and assorted according to quality.

(b) "*Soda Ultramarine*" is sometimes made with soda alone (either carbonate or caustic), and at others with a mixture of soda and sulphate of soda. Rowland Williams found the following proportions of the respective ingredients to answer satisfactorily :—

	Per cent.
China clay .. .. .. .. .. .. ..	36·8
Carbonate of soda .. .. .. .. .. .. ..	36·8
Sulphur .. .. .. .. .. .. ..	22·0
Coal .. .. .. .. .. .. ..	4·4
	<hr/>
	100·0

The proportions for soda and sulphate of soda ultramarine have been previously given under "sulphate ultramarine." The ignition is carried on in a manner similar to that already described. The resultant green product, owing to its avidity for oxygen, is partially changed into ultramarine blue by simple contact with the air. It is entirely converted into the blue variety by roasting with an additional quantity of sulphur. With care, ultramarine blue may be manufactured in one operation, by increasing the proportions of soda and sulphur.

(c) "*Silica Ultramarine*" is manufactured in the same way as soda ultramarine, except that, in addition to the other materials, silica to the extent of 5 or 10 per cent. of the weight of clay is employed. By this process, ultramarine blue of a slightly reddish tint is obtained in one operation. The method has, however, one decided drawback, viz. that the materials employed are rather liable to fuse during ignition. The faintly reddish hue of "silica" ultramarine becomes more intense according to the proportion of silica

present. "Silica" ultramarine is said by some to be less readily attacked by acids and by strong alum solutions than ultramarine prepared by the "sulphate" and "soda" processes; but Rowland Williams' experience does not confirm this statement. He mentions that good artificial ultramarine withstands the action of weak acids much better than is generally imagined. He had occasion to test many samples which resisted the action of dilute acids to a remarkable degree. Most strong acids, of course, decompose both artificial and native ultramarine, with evolution of sulphuretted hydrogen. Native ultramarine is, however, less susceptible to the influence of acids (both strong and dilute) than the artificial compound. This difference of behaviour is probably due to the fact that the former contains considerably less sulphur than the latter, and it is also possible that the constituents of natural ultramarine may be combined in a somewhat different manner from those of the artificial product.

Notwithstanding the large amount of research with reference to the chemical composition of ultramarine, the origin of its blue colour still remains in doubt. According to Wilkens (*Ann. Ch. Pharm.*, xcix. 21), ultramarine consists of two portions, one of which is easily attacked by hydrochloric acid, and is regarded by him as the essential constituent, whilst the other portion is insoluble in hydrochloric acid, and contains variable proportions of clay, sand, oxide of iron, and sulphuric acid. From his analyses of the pure blue, Wilkens deduces the formula  $(2\text{Al}_2\text{O}_3 \ 3\text{SiO}_2)$   $(\text{Al}_2\text{O}_3 \ 4\text{SiO}_2)$   $\text{Na}_2\text{S}_2\text{O}_3 \ 3\text{Na}_2\text{S}$  :—

										Per cent.
Silica ..	..	..	..	..	..	..	..	..	..	37·6
Alumina ..	..	..	..	..	..	..	..	..	..	27·4
Sulphur ..	..	..	..	..	..	..	..	..	..	14·2
Soda ( $\text{Na}_2\text{O}$ ) ..	..	..	..	..	..	..	..	..	..	20·0
										—
										99·2

Wilkens regards the blue colouring principle of ultramarine as a compound of hyposulphite and sulphide of sodium. He

considers the presence of iron is not necessary for the production of the blue; whilst Dr. Elsner, in a paper published in 1841, states that about 1 per cent. of iron (which he presumes to be in the state of sulphide) is essential. Rowland Williams asks whether it is not conceivable that the blue colour of ultramarine may be due to the presence of a small quantity of black sulphide of iron, most intimately combined with a colourless or comparatively colourless compound (such as white ultramarine), the whole mass (owing to the dilution of the black sulphide) showing a blue reflection.

Ultramarine is insoluble without decomposition in any known menstruum. According to P. Ebell (*Ber.* 16), ultramarine, when in the most finely divided state, will remain suspended in pure water for months. The liquid may be filtered unchanged through several layers of Swedish filter paper, and appears perfectly clear when examined in a  $\frac{3}{4}$  in. layer, and on evaporation deposits the ultramarine as a lustrous coating on the sides of the vessel. Rowland Williams repeated the above experiment, and can confirm Ebell's statement. This result shows the necessity of due precautions being taken during the washing of the ultramarine in the process of manufacture, otherwise a considerable amount of the finely divided blue may be lost. Ultramarine is largely used in calico printing for pigment styles, being fixed on the fibre by means of albumen. It is also employed for blueing linen and cotton, wax candles, lump sugar, &c. Ultramarine is not adulterated to a large extent, the chief sophistication being barium sulphate (barytes), and occasionally chalk and china clay.—(Rowland Williams, in *Industries*.)

Another writer in *Industries* says that the manufacture of ultramarine has perhaps hardly received the attention it deserves in England. The importance of the industry has been recognised in Germany, however, and though the palmy days of the trade, when the whole production was in the hands of a few firms, and the price was a matter of

private friendly arrangement, are gone for ever, yet the business is in a flourishing state, and should prove lucrative if properly managed. It is a characteristically English failing to overlook branches of business not dealing with large quantities of staple commodities, and thus many of the smaller but remunerative industries have passed out of our hands. When one observes that almost every sheet of ordinary blue official paper is decolorised when accidentally brought into contact with an acid, betraying the fact at once that its colouring matter is ultramarine, one realises that a very considerable consumption for this and similar purposes must take place. Like most trades based upon chemical principles, the manufacture of ultramarine has recently made rapid strides, and some of the latest developments are recorded in a paper by J. Wunder, appearing in a recent number of the *Chemiker Zeitung*, which is worthy of some attention.

With most people not directly interested in it, the term ultramarine is taken to mean the *blue* pigment known under that name, the words being reckoned almost synonymous. Others, more erudite, recognise the existence of a green variety, but that the production of such colours as red and violet is possible is scarcely suspected. Of course the blue is the most important, but even that does not correspond to one specific substance, products of different shade being prepared by modifying the process of manufacture. As usually made, ultramarine is formed by heating together carbonate of soda, kaolin, sulphur, and charcoal, with limited access of air, the resulting pigment being green; this, on roasting with sulphur, becomes blue. If the operation be conducted with complete exclusion of air, so-called ultramarine white (in reality grey) is produced, which becomes green on further heating. Ultramarine blue capable of resisting the action of alum is sometimes required, and may be obtained by the use of a highly silicious charge and much sulphur, the burning being conducted in crucibles or

in mass according to the purpose for which the pigment is required. The former process is costly, while the latter gives a product containing a good deal of free sulphur, which is objectionable for such purposes as calico printing. Removal of the excess of sulphur by heat or caustic soda is not feasible, as the colour suffers in either case, but a certain amount of success has attended experiments with sodium sulphide, the colour often brightening noticeably.

It is curious that chemically pure sodium carbonate, or such as is made by the ammonia-soda process, is not well fitted for the manufacture of ultramarine; Leblanc soda, containing a little caustic, is distinctly preferable. Sprinkling the soda with a strong solution of sodium sulphide before use is a good plan, and one easy to adopt. The more silicious the mixture the more difficulties are encountered, but the product is a deeper, richer colour, and withstands the action of alum and weak acids better. Excess of oxygen must be guarded against; many a manufacturer has had a batch turn out a hard cold blue, instead of a soft rich colour, solely on account of a too-excellent draught, an accident especially liable to happen in winter time. So much dreaded is this catastrophe that some makers habitually limit the air supply—smothering the neighbourhood with smoke, and wasting coal. The need for exact control here indicated points to a probable advantage from the use of gaseous fuel. Considerable economy has resulted from the use of the waste gases from one furnace serving for the preliminary heating of another; a better plan would probably be the introduction of regenerative heating.

The crude ultramarine as it comes from the furnace contains a large proportion of soluble salts, notably 20 to 24 per cent. of sodium sulphate, which have to be removed before it is merchantable. Usually, after grinding, it is simply stirred up repeatedly with hot water and the aqueous extract is siphoned off. That such a crude method should be in vogue at the present time is very significant of

the ample margin of profit that must exist. By systematic extraction and filtration under pressure the washing may be effected with so little water that the solution is sufficiently concentrated to pay for evaporation by the heat of waste furnace gases, the recovered sodium sulphate serving to replace part of the raw material.

The quality of ultramarine largely depending upon its fineness, it is graded by levigation, the coarser portions being filter pressed, and the finest "floating" quality, which remains in suspension for an inconveniently long time, precipitated by the addition of a trace of an ammonium salt, gypsum, or even hard water, and filtered by the aid of a suction tube on the principle of an ordinary Bunsen pump.

The first successful attempt to produce ultramarine *violet* was made by Professor Leykauf in 1859. By heating ordinary ultramarine with calcium chloride in the presence of air and moisture, he obtained a violet-toned pigment, but it was not a full colour. The active substance in this change was probably hydrochloric acid, produced by the decomposition of the calcium chloride. Later experiments with other reagents, such as chlorine and gaseous hydrochloric acid, led to the following methods being devised. In the first, ultramarine blue is spread out on stoneware shelves in iron chambers and treated with a mixture of chlorine and steam at a temperature of 300° F. to 480° F. for about three hours. In the second, the plant is very similar, but at the bottom of the chambers are stoneware dishes, into which hydrochloric acid is poured from time to time. As the temperature is raised, copious vapours arise from these, evaporation being aided by a strong draught, and the ultramarine blue, after being kept at 428°–446° F. for some seven hours, becomes converted into a dull violet, which brightens on continuing the process with a temperature gradually falling to 320° F. The ultramarine violet produced by either of the above methods resists the action of lime, and is of general applicability.

The pigment produced by a third and simpler process, consisting merely in heating ultramarine blue mixed with salammoniac and a little sodium nitrate, is unfortunately not so stable. Another shade of considerable interest is a pure bright light blue, formed by heating the violet variety in hydrogen to about  $536^{\circ}$ - $554^{\circ}$  F. It has not yet been prepared on a commercial scale, but certainly merits the attention of manufacturers. An ultramarine red has been made by acting on the violet produced by either of the first two methods with the vapour of either nitric or hydrochloric acid at  $275^{\circ}$ - $293^{\circ}$  F., the sole essential determining condition being the temperature. Iron vessels could be used in the case of nitric acid at this temperature, but if hydrochloric acid were employed stoneware would have to be substituted. In the manufacture of the violet the temperature is above the limit at which hydrochloric acid acts on iron.

It is now only necessary for some successful experimenter to put on the market yellow and orange shades of ultramarine for almost the whole of the spectrum to be represented. The problem of the cause of the colour of ultramarine, attempts to solve which have been repeatedly made, seems increasingly difficult when its protean character is considered; but this from the industrial point of view is of secondary importance, provided all required shades can be produced with ease and economy. Nevertheless, it is certain that here, as in other cases, substantial technical progress would follow from adequate scientific investigation.  
—(*Industries.*)

Ultramarine was also made the subject of a very interesting paper, by Herbert J. L. Rawlins, read before the Society of Chemical Industry, in December 1887.

After referring to the native form, lapis lazuli, Rawlins goes on to observe that "analysis could give no clue as to the cause of the blue colour. To prepare it artificially became a great object, and the efforts in this direction were

stimulated by the offer of prizes, amongst which was one of 6000 francs, offered by the 'Société d'Encouragement' of France, to be awarded to the discoverer of a method of making ultramarine, provided it did not cost more than 90s. per lb. How strange it seems to think of this in these days when the value has fallen to less than half that price per cwt.!

"As early as 1814, two German chemists, Tessärt and Kuhlmann, had observed the formation of a blue product in soda kilns and calcination kilns, but Guimet, in 1828, first discovered how it was produced, and gained the 6000 francs prize. He did not, however, publish his method, and grew immensely rich, although the price sank to about 16s. per lb. In 1828 he was producing at the rate of 120,000 lb. annually.

"About the same time, or, as is positively asserted by some, even prior to Guimet, Gmelin made the same discovery and published his researches in full, thus perhaps laying the foundation stone of the present supremacy of Germany in this manufacture.

"In spite of the valuable discoveries of Hoffmann, Unger, and others, our knowledge of the chemical constitution of ultramarine is very limited and uncertain, many different theories having been advanced regarding the cause of the blue colour.

"According to Wilkins, ultramarine is composed of two portions, one of which consists of two silicates of alumina with sulphite and sulphide of sodium, and is constant in its composition; the other being a mixture of variable quantities of sand, clay and oxide of iron, with sulphuric acid. The blue colouring principle he considers to be a compound of sodium sulphite and sulphide. Another ingenious theorist, Stein, in two papers published in the *Jahresberichte* in 1871 and 1872, concludes that blue ultramarine contains sulphurous, and not thiosulphuric acid, that neither sulphites nor thiosulphates are necessary to its composition, and that it owes its colour to the presence of black sulphide of

sodium, which is formed at high temperatures by the action of sulphide of sodium on alumina—admitting, therefore, that it is not a chemical compound, but merely a mechanical mixture, the blue colour of which is due to the bodies composing it.

“ Brunner considers ultramarine to be a compound of aluminium silicate, with sodium sulphate and sulphide; while Brünnlin regards it as a double silicate of aluminium and sodium, in combination with pentasulphide of sodium. Green ultramarine he considers to be the same double silicate in combination with bisulphide of sodium.

“ Again, according to Ritter, ultramarine contains a double silicate, not only associated with polysulphide, but also with thiosulphate of soda; and Schülzenberger, on the other hand, considers that it is a mixture of a double silicate with sulphite and monosulphide of sodium.

“ Endemann considers that the blue colour is due to a ‘colour nucleus,’ consisting of unchanging proportions of aluminium, sodium, oxygen and sulphur, in each variety of ultramarine the proportion being different, while the rest of the sodium and aluminium and the whole of the silica merely act as a vehicle necessary to the preparation and existence of the colour. He considers that this ‘colour nucleus,’ in the case of white ultramarine, which he calls the ‘mother-substance in the manufacture of blue ultramarine,’ has the formula  $\text{AlNa}_4\text{O}_2\text{S}_2$ . By the action on two molecules of this of sulphurous acid gas,  $\text{Na}_2\text{O}$  is removed, and green ultramarine  $\text{Al}_2\text{Na}_6\text{O}_3\text{S}_4$  is formed, which then, by the action of oxygen, which forms sodium sulphate, passes into the pure green compound, having the formula  $\text{Al}_2\text{Na}_4\text{O}_5\text{S}_3$ . In the ‘indirect process’ of manufacture, green ultramarine is converted into blue by being burned with sulphur. By this means Endemann considers that more sodium and sulphur are removed, and blue ultramarine  $\text{Al}_2\text{Na}_2\text{O}_3\text{S}_3$  is formed. He considers that the other portion, not included in the ‘colour nucleus,’ differs in different samples. In

one which he mentions it has about the composition  $3\text{Al}_2\text{O}_3 \cdot 5\text{Na}_2\text{O} \cdot 16\text{SiO}_2$ .

"But of all chemists who have worked on this subject, none has done more to increase our knowledge of 'the blue marvel of inorganic chemistry,' as he himself has called it, than Reinhold Hoffmann. His position of manager of the Marienberg Ultramarine Works, near Bensheim, in the Grand Duchy of Hesse, renders his acquaintance with the manufacture perfect, and his untiring researches on the subject have been well rewarded by results both interesting and valuable. He considers ultramarine to be a double silicate of sodium and aluminium, together with bisulphide of sodium, the variety poor in silica, characterised by its paleness and purity of tint, and easy decomposition by acids, having the formula  $4(\text{Al}_2\text{Na}_2\text{Si}_2\text{O}_8) + \text{Na}_2\text{S}_4$ ; while that rich in silica, characterised by its dark and somewhat reddish tint, and more difficult decomposition by acids, has the formula  $2(\text{Al}_2\text{Na}_2\text{Si}_3\text{O}_{10}) + \text{Na}_2\text{S}_4$ . He also considers it very doubtful whether green ultramarine is really a chemical compound, and indeed it is now generally considered that the colour is only due to small traces of sodium salts in very intimate mechanical mixture with the blue variety, for by heating the green body for some time at  $160^\circ$  with water in closed tubes, it is converted into the blue product, and small traces of sodium compounds are found in solution in the water; and further, on heating blue ultramarine strongly with sodium sulphate and charcoal—that is, acting upon it with sodium sulphide—the green variety is formed.

"In a paper by Knapp, an abstract of which appeared in the *Journal of the Chemical Society* for March 1880, there are some curious facts recorded with regard to the colouring agent. It was noticed that when silicic acid was replaced by boracic acid, a blue, nearly as stable in its properties as that of ordinary ultramarine, was produced. It was found that a blue could be obtained without alumina being intro-

duced. Hence silica without alumina, and alumina without silica, can be employed with a certain amount of success. The blue, however, formed without silica, is not so strong or stable as that formed with it.

"One very curious property which ultramarine possesses is its power of giving up its sodium in exchange for other metals. Thus, by heating blue ultramarine with a concentrated solution of silver nitrate in sealed tubes to  $120^{\circ}$  for fifteen hours, a dark yellow *silver* ultramarine is produced, containing about 46.5 per cent. of silver. This corresponds to about 15.5 per cent. of sodium, which is just about the amount that the original body contained.

"When this body is heated with an aqueous solution of sodium chloride to  $120^{\circ}$  in sealed tubes, about three-quarters of the silver is replaced by sodium, but the other quarter cannot be so replaced; in fact, blue ultramarine, when heated with silver chloride, takes up silver, and becomes green. But by heating silver ultramarine with sodium chloride in the dry way, at rather a higher temperature, the whole of the silver is replaced by sodium, but the ultramarine thus regenerated does not equal the original body in colour. The change is probably due to the loss of sulphur in the formation of the silver ultramarine.

"If in the above experiment potassium chloride be substituted for the sodium salt, and the temperature not allowed to exceed  $400^{\circ}$ , a bluish-green *potassium* ultramarine is formed. *Barium* ultramarine is a yellowish-brown product, *zinc* ultramarine is violet, and *magnesium* ultramarine is grey. These may all be obtained by acting on the yellow silver ultramarine with the corresponding metallic chloride.

"From the experiments of Dollfus and Goppelsröder some very striking differences have been brought to light between the three types of colour which they examined—namely, the blue, green and violet—in their behaviour with various reagents. Thus, an aqueous solution of caustic soda or

potash does not act on the blue or green, but turns the violet to blue, and when heated with carbonic oxide the same result ensues. Many other reagents have the same effect on the violet variety, but when acted upon with sodium sulphide, the green turns grey, and when heated with potassium chlorate becomes darker and loses its brightness of colour. Dollfus and Goppelsröder attempt no explanation of these facts, but simply state them as results of their observations, and profess their inability to give any chemical formulæ for the three ultramarines, though they consider that there is sufficient proof that each has its distinct constitution. They give as their opinion, however, that they are double silicates of aluminium and sodium, in which a part of the oxygen is replaced by sulphur.

"Violet and red ultramarines are more bodies of scientific interest than of any practical use, as their colouring power is not sufficiently great. The violet variety may be prepared by exposing the underground blue product to chlorine gas under a high temperature, while the red may be obtained from the violet by acting on it, under a low temperature, by dilute nitric acid fumes.

"The first artificial method of producing ultramarine was that known as the 'indirect process'—that is, first the manufacture of green ultramarine; and secondly, its conversion into blue. It was carried out as follows:—

"An intimate mixture of Glauber's salts, china clay, and coal or rosin, finely ground together, was placed in crucibles and baked or burned in an oven for about six hours. It was then transferred to iron trays, and heated with flowers of sulphur to the point where the sulphur took fire, when it was allowed to burn itself out. By this second process the green was converted into blue. It was then washed, ground with water, and settled out, the first deposit being of a darker shade than the second, and the colour becoming lighter as the powder settled was finer in grind. This is

essentially the method employed now at many German works—those at Marienberg, for instance—and produces what is known as “sulphate ultramarine,” distinguished by its pale shade and almost *greenish* blue tint.

“There are, however, some objections to the indirect process, and it was considered advisable to find a plan by which ultramarine could be made in bulk in a muffle furnace. The following is a method which is employed at the present time in some of the German works:—

“A mixture of china clay, carbonate of soda, sulphate of soda, sulphur, sand and charcoal or rosin, finely ground together, are placed upon the floor of a muffle furnace, being pressed down so as to present an even surface. The mixture is then entirely enclosed with fire-clay tiles, the spaces between which are filled in with thin mortar. When the oven is so charged, the front is built up, a small hole being left for watching the temperature of the flue between the tiles and the top of the furnace, and for drawing samples during the process, which is done through a corresponding hole in the front of the fire-clay tiles, temporarily closed with a fire-clay stopper. The oven is now heated, slowly at first, and afterwards more strongly, so that at the end of eight or nine hours it is at a dull red heat. It is kept at this temperature for about 24 hours, when the heat is raised so that a clear red glow is obtained, which is kept up to the end of the operation.

“For the purpose of taking a sample, an iron spoor borer is introduced through the hole left in the enclosing tiles, turned round, and pulled out. The contents are laid on a clean tile, and quickly covered with another tile, on which a second quantity is placed, and allowed to remain exposed to the air. If the oven has been sufficiently heated the covered sample should appear of a bluish green, and no longer brown or yellow, while the second sample should be rather bluer. If this be the case, the oven is heated slowly for another hour, and then all communication with the outer air is cut off. It

is allowed to cool and then opened, when the contents should appear as a beautiful blue mass, the lower portion of which, however, is of a greenish tinge. Both parts are now treated alike, but worked up separately, the greenish-blue portion making an inferior article. The finishing process is as follows:—

“The raw ultramarine is ground in upright mills, and then repeatedly boiled for about ten or fifteen minutes at a time in cast-iron boilers, being all the time agitated by a mechanical stirring arrangement. It is then allowed to settle, and the water is drawn off with a siphon. As soon as the powder settles into a hard compact mass, it has been sufficiently washed, and it is then dug out. The part next to the bottom of the boiler is generally coarse and of poor quality. It is carefully separated from the upper portion, which is transferred to wet mills of the ordinary description, and there ground for six to twelve hours, during which time about 150 lb. can be treated in each mill. The ground colour from these mills is then collected in a large tub, and allowed to settle for four hours, during which time the coarsest particles fall to the bottom. The liquid is then passed through a series of tubs, in each of which it is allowed to stand for a period of time, lengthening as the quality settled out becomes finer, the last settling requiring about three weeks. The various qualities are then dried and sifted, when they are ready for the market.

“The blue produced by this operation is of a good quality, but there are some objections to the process, which have given rise to another, in which the ultramarine is produced direct in crucibles similar to those used in the indirect process.

“This is conducted as follows:—The mixture of raw materials consists of about 100 parts of china clay, 90 of carbonate of soda, 110 of sulphur, 20 of charcoal, and a quantity of infusorial earth, varying according as the ultramarine produced is desired to be rich or poor in silica.

These are finely ground together, in which process great care must be observed, as much depends upon its being properly carried out. The mixture is then filled loosely into crucibles provided with flat circular lids, which are fixed on with mortar containing clay. This is allowed to dry, and the crucibles are then ready for firing, which process is conducted in ovens, generally constructed so as to contain several hundred crucibles, which are arranged in rows one above another.

"The mixture undergoes a very curious change of colour while in the ovens. When put in it is greyish white, and during the process of burning it becomes successively brown, green, blue, violet, red and white, in the order named. These changes are, according to Guimet, due to oxidation. The brown appears with the blue flames due to the combustion of the sulphur, the green just after the sulphur flames have ceased, and the blue is first formed at a temperature of about 700°—i. e. a bright red heat. If, after this, heat be still applied and air freely admitted, the mixture becomes first violet, then red or rose coloured, and finally white. When this white body is heated to redness with carbon or other reducing agents, the red, violet, blue, green and brown colours (according to the amount of reducing agent employed) may sometimes be reproduced, though the reaction is by no means a certain one.

"If brown ultramarine be removed from the oven, and allowed to remain exposed to the air, it immediately takes fire and burns to an inferior blue colour. The same thing occurs with the green body. Even if the brown product be completely cooled before being exposed to the air, it will, as soon as the air is allowed to reach it, get hotter and hotter, until it is glowing, when it will burst into flame and become blue. Attempts have been made to preserve the brown colour, which is of a beautiful chocolate tint, but have always failed. In one instance, when this was tried, the colour was put immediately into water, and treated like the ordinary blue variety, and as long as it was kept moist no change was

apparent. After being washed and wet ground the moist powder was put into a cask, where for some time it was allowed to remain undisturbed. At the end of about three weeks it was noticed that the mass was hot, and on being turned out of the cask and broken up it was found to be at a glowing heat in the interior.

"After the oven has been fired for several hours, it is carefully closed at every point where air might enter, and allowed to cool for four or five days. The exact length of time during which the ovens are fired, and the amount of air admitted, depend upon various circumstances, one important one being the state of the weather. Thus, on a dull, foggy day, when the draught in the chimney is not good, a longer time is required. Of course, no rule can be given for this, and it is the experience required in the management of the oven that makes the manufacture so difficult to carry out successfully, the early efforts of a manufacturer not unfrequently resulting in the loss of a whole ovenful of raw material. As soon as the oven has cooled, the crucibles are taken out, and the contents of each are turned out in a solid mass, which must be carefully cleaned with a knife of any badly burned portions, and afterwards broken up and thrown into a cask along with the contents of other crucibles.

"This forms what is known as crude raw ultramarine. It contains about 15 per cent. of sulphate of soda, which must be removed before the colour is fit for sale.

"For this purpose it is washed with hot water in large tubs, after which it is ground in wet mills to an impalpable powder, and allowed to stand for about an hour in a large tub, in order to remove the coarsest particles and dirt which are sure to be present. It is then removed to another tub, where it settles for four or five hours, and from this it passes to others, where it stands for various lengths of time, increasing, of course, as the powder to be settled becomes finer, the last settling occupying three or four weeks, and

producing the strongest quality that can be obtained—that is to say, it will bear mixing with more of a reducing medium, such as mineral white, than would a former settling for the mixture in each case to be of the same depth of colour.

“The water, after the final settling, still contains about 5 per cent. of ultramarine. This would take five or six months to settle, and as this time could not generally be given to it, it is precipitated with lime water, which has a sort of coagulating influence upon the particles, which can then be removed by filtration. It is a curious thing that this last quality is quite different from the one preceding it, being very inferior in both colour and strength.

“After settling, all the various qualities are dried in kilns, and sifted through fine brass wire sieves by means of a fan, which breaks up the lumps and forces the particles through the meshes of the sieve, which must be very close—about 100 to the inch—in order that the ultramarine may be perfectly smooth and free from lumps or grit of any sort. When finished, it should be in the form of an impalpable powder—the finer qualities so fine, indeed, as to feel almost *buttery* when rubbed between the fingers. After this process the different qualities and shades are mixed to certain standards, and are then ready for sale.

“The uses of ultramarine in the arts and manufactures are very numerous and important. The most important, from the point of view of quantity, is the manufacture of ‘square blue’ for washing purposes. In the preparation of this article the ultramarine is generally mixed with bicarbonate of soda and some glutinous material, to help it to retain its shape, and is then pressed into the well-known form of small square or oblong blocks.

“It is also used largely in the manufacture of blue paint and printing ink, and in the preparation of blue mottled soap. The way in which it is employed in the last-named manufacture is worthy of remark. It is added to the soap while it is in a molten state and just before it is allowed to

cool, and thoroughly mixed with it, so that the whole mass is of a pale blue tint. If a small quantity of this be removed from the boiler and cooled quickly, it remains of a uniform tint, but in the case of the whole boilerful, where the cooling is very slow, the action is entirely different. Just at the point of cooling, when the soap is going to set hard, the ultramarine—to use a technical expression—"strikes," and goes into the form which gives to blue mottled soap its well-known appearance.

"In the manufacture of paper, ultramarine also plays an important part. It is here used not only for producing blue shades, but also as a bleaching agent, to counteract the yellow when white paper is made.

"Another important use is in the calico manufacture, where it is used both in the printing of blue patterns and in the finishing of goods. In the case of calico printing, it is mixed with albumen and printed on to the calico, which is then subjected to the action of steam, the albumen being by this means coagulated and each grain of ultramarine surrounded by an insoluble envelope, so that it cannot be washed out of the calico.

"The growth in the manufacture of ultramarine has been very remarkable, especially when it is considered how little the process is understood chemically, and what care and patience—to say nothing of the equally important item of capital—are required in the starting of a manufactory. Commencing less than 50 years ago in the works of Guimet, at Lyons, who produced 120,000 lb. annually, there are at the present day nearly 40 manufactories at work in various parts of the world—chiefly in Germany—producing about 20 million lb. per year. The following figures will give some idea of ten years' growth of this industry—from 1862 to 1872:—

	1862.	1872.
Number of manufactories .. .. ..	24	32
Men employed.. .. .. ..	964	1929
Tons manufactured.. .. .. ..	3556	8585

"From the above numbers it will be seen that in these ten years the manufacture more than doubled itself, the fact being due, however, not so much to the increase in the number of works, which was only one-third, as to the enlarged capabilities of those existing in 1862. Thus, in the works of Dr. Leverkus, near Cologne—the first works ever started in Germany—the number of men employed had, during these ten years, more than doubled, while the output had trebled; and in the case of the Marienberg Works the difference was even more striking, the number of hands employed and the quantity turned out per annum having nearly quadrupled."

In reply to various questions which were asked in the discussion which ensued, Mr. Rawlins said that, with regard to the use of ammonia soda, it had frequently been used in the manufacture of ultramarine, and was constantly used he understood, but he himself had not much experience of it. As far as he could make out, it certainly produced ultramarine, but of a darker shade than that made with Leblanc soda. It could not be supposed, in works where the Leblanc soda was used, that ammonia soda could conveniently be substituted, for of course a works when established had to adhere to its known standards and shades, and it would not do to change the raw materials, though the ammonia soda produced a very good ultramarine. As regards the discovery of ultramarine, the first works started anywhere were Guimet's. He had with him a little historical list containing the dates at which the various works established before 1866 or a little later had been started. It was drawn out by Hoffmann, who, as he stated before, was the manager of large ultramarine works, and he put down Guimet's, which were started in 1829, first on the list. Dr. Leverkus started in 1834. He knew that the discovery of ultramarine had been attributed to different people. He had mentioned Guimet because it had generally been considered, as far as he had heard, that Guimet and Gmelin were the two who discovered it from a manufacturing point of view. He had heard of crystals of ultra-

marine, but had never seen any, and he knew they were very difficult to prepare, and very rare. He had mentioned that the grinding had to be done very thoroughly, because the better it was mixed and the finer it was ground, the better was the ultramarine produced. If it was badly mixed it was quite fatal to getting a good result. Grinding lightens the colour. Raw ultramarine must be ground before it was practicable to use it at all. For instance, a coarse ultramarine could not be used for printing calico. Therefore it was necessary to grind it both for the sake of the colour and for the sake of the way in which it was applied. It was increased in value by grinding because it made it stronger and finer. Before grinding it was of a dark colour, but after grinding it became lighter and brighter.

The materials employed in McIvor's process for making ultramarine are kaolin or other suitable clay, a solution of sulphide of sodium, in which sulphur in the form of flowers of sulphur is dissolved to saturation, and caustic or carbonate of soda.

The preparation of the solution is effected by adding the sulphur to boiling sulphide of sodium liquor of maximum strength until it ceases to be taken up. The clay and soda are first roasted together at a red heat, so as to effect a partial double decomposition, and the product, after grinding, is made into a thick paste with "sulphur liquor," i. e. the sulphide of sodium solution of sulphur. This latter operation may be carried out in an ordinary pug-mill. The paste so formed is dried in an oven or other convenient way, and the dried mass (being broken into small pieces) is roasted without access of air in a closed earthenware retort, first at about  $480^{\circ}-570^{\circ}$  F. for an hour, then at a red heat for eight hours, and finally at a moderate heat just below dull redness, in presence of a slow current of air, which enters through a series of holes or small openings in the front of the retort, the current being regulated by means of a damper or an adjustable slide. The retort should be allowed to become quite

cold before being opened, otherwise the tint of the product will be injured.

McIvor has found the following proportions of the raw materials used in the process to yield excellent results, viz:—

Sulphide of sodium .. .. .. .. ..	42 lb.
Sulphur .. .. .. .. .. ..	20 "
Kaolin (china clay) .. .. .. .. ..	110 "
Soda (as carbonate) .. .. .. .. ..	106 "
or	
Caustic soda .. .. .. .. .. ..	40 "

These quantities yield about 2 cwt. of ultramarine blue.

The following communication from the pen of J. B. Nejedly, of Vienna, appeared in the *Chemiker Zeitung*, during 1888:—

“ Animated by various articles and notes in your journal under the heading of ‘The Present Position of the Manufacture of Ultramarine,’ I would like to draw out of obscurity a little work on this industry which contains much that is true, and furnishes at the same time many comparisons with regard to the present position of the ultramarine industry in Germany.

“ The work above referred to was printed in the year 1840 and bears the title:—

“ ‘Treatise on the chemico-technical preparation of Ultramarine colours, according to the discoveries of Leykauf and Heyne, or on the importance of the manufacture of blue and green Ultramarine for purposes of science, art, and industry. By Friedr. Wilh. Heyne, president of the Nürnberg Ultramarine Manufactory.

Nürnberg: 1840. Printed at the Campe Press.’

“ The preface, which I consider to be well suited to present circumstances, I reproduce verbatim, while from the little work itself I will only quote such sentences as would seem to be suited to the present time, and which are the most important as bearing on the subject.

“ ‘Preface.—The incitement to this treatise was furnished

by the utility of the discovery of Leykauf, instructor of chemistry at the technical schools in Nürnberg, of artificially preparing the well-known blue mineral colour styled ultramarine, according to simple principles, which discovery was supplemented by the production of the green ultramarine, an equally genuine and beautiful green mineral colour, by the technist Heyne in Nürnberg. A short review of the importance of these two discoveries for mankind in general and for science, art, and industry in particular, will form the main subject of this treatise, which has no other object but that of arousing the attention of all high protectors and stimulators, as well as friends of industry and art, to a newly-born industrial branch. At this moment we are living in a period when many industries have got into the stocks, in consequence of far too severe competition, combined with other influences ; indeed they are barely able to support those engaged in them. If in consequence of this state of things it already becomes of the most vital importance that fresh sources of acquisition should be obtained, it becomes all the more so when by their means at the same time materials come into requisition which the Fatherland possesses in great superfluity, and which otherwise possess no intrinsic value beyond just the expense of extracting them from their natural localities or deposits, and the worth that attaches to their working up for industrial purpose. A source of acquisition in this sense is met with in the manufacture of blue and green ultramarine colours, which in course of time can be raised to an extremely valuable acquisition. May the communications here made result in their being considered worthy of a thorough many-sided investigation and consideration.'

#### " REGARDING THE WORK ITSELF.

"Page 21.—'Not long since a prize of 6000 francs was offered by the "Société d'Encouragement." This prize was gained by Guimet, who has not published his process, and

who now furnishes ultramarine at the price of 25 francs per oz., whereas it otherwise cost 200 francs per oz. Latterly, in 1839, Guimet reduced his price for ultramarine, viz. No. 1, for painting, to 10 francs, a lighter shade being 6 francs per oz. In addition, this manufacturer furnishes lower qualities for carpet and paper manufacturers at 20 francs and 12 francs per lb.'

"Page 23.—'Indeed, if we are able to produce ultramarine by means of a polysulphide of sodium and common clay, then the most beautiful and most lasting of all known blue colours would at the same time become the cheapest of them all.'

"Page 27.—'All faults which are known to exist in the old methods are obviated in the new invention of Leykauf and Heyne, while the same offers the following advantages:—

"(1) The materials which are treated with it can be brought into use without any special previous chemical preparations, indeed as supplied by Nature, while chemical treatment is entirely unnecessary. In view of the unimportant cost of derivation of the raw material, there cannot consequently be any questions raised with regard to waste.

"(2) This method is so simple that any man of sound intellect can easily work it, without possessing any special chemical knowledge beforehand. As the labour can be easily grappled with, errors can only occur when the grossest carelessness is shown in conforming to the instructions prescribed.

"(3) According to the said method one can work according to any desired scale, and, what is best of all, the larger this scale the more favourable are the results obtained, lighter work and excellence of quality.

"(4) If the process is carefully conducted, everything is in your own power, nothing depending on chance.

"(5) Consequently an equal product can invariably be obtained, while this can at will be brought to the most

complete stage of perfection at but little greater cost than lower qualities entail.

““(6) According to this method you are master of the fire, enabling a retention of colours in any desired shade, of the deepest tone, of the greatest permanency.

“From this it appears: That this process is the easiest, the cheapest, and the most complete. Worked according to this method the hope is likely soon to become a reality that ultramarine may yet become the cheapest of all mineral colours, and as in the same everything rests upon simplicity, the preparation of the article in future will be carried on somewhat after the fashion of baking, brewing, &c.”

“Page 32.—‘Moreover, there is not only blue ultramarine, but also a pure green, and we may venture the hope that similar combinations in white, black, red, and yellow will soon follow in equal perfection. In consequence of these discoveries, Leykauf and Heyne have erected a factory in Nürnberg, which, according to a circular dated 15th July, 1840, is in operation under the style of “Leykauf, Heyne and Co.” and are producing the two ultramarine colours referred to at the present time at the rate of 50 lb. per day.’

“Page 33.—‘All the mechanical appliances of the factory are at the present time exclusively worked by hand, the number of persons employed being sixteen; while the establishment upon completion of the buildings that are wanting is calculated to employ twenty operatives and two horses. With this extension the factory will be able to turn out 5 cwt. blue and 5 cwt. green weekly, consequently annually 500 cwt. of finished merchantable ultramarine will be brought on the market.’

“Page 35.—‘Now, as regards the prices ruling at present for Nürnberg ultramarine, these are, as compared with those of the French, more than 500 per cent. cheaper. Blue ultramarine costs, namely, in Nürnberg, quality No. 0, 10 florins per lb.; a lighter quality, which is nevertheless darker than the darkest French at 100 francs, 5 fl. per lb.; a third quality

likewise darker than the seconds French at 60 francs, 3 fl. per lb. Green ultramarine, 3 fl. 10 kr. per lb.

“ How much further, however, these low prices will be yet reduced after the completion of the factory, may be gathered from a detailed calculation of cost which the chief of this factory has made himself responsible for as being the highest estimate. This calculation of cost is based upon the weekly production of 10 cwt., which the factory will soon be able to turn out, and upon a necessary cost of plant and working capital of 90,000 Rhenish florins, as follows :—

“ Page 36.—‘ Calculation of cost of 500 cwt. blue and green ultramarine :—

	Fl.
(1) Raw material and cost of transport .. .. .. ..	10,000
(2) Fuel, including cost of transport of 7200 cwt. of coal at fl. 1.30 .. .. .. .. .. ..	10,800
(3) Wages of 20 operatives at fl. 250 per annum ..	5,000
(4) Utensils and apparatus.. .. .. .. .. ..	3,200
(5) Buildings and repairs .. .. .. .. .. ..	3,400
(6) Keep for two horses .. .. .. .. .. ..	600
(7) Expense of factory .. .. .. .. .. ..	3,000
(8) Cost of administration .. .. .. .. .. ..	2,000
(9) Unforeseen matters and accidents .. .. .. ..	2,000
(10) Interest on building and working capital at 5 per cent. .. .. .. .. .. ..	4,500
(11) Public taxes, insurance, &c. .. .. .. ..	500
Thus 500 cwt. will cost .. .. .. ..	Fl. 45,000
” 1 ” ” .. .. .. ..	Fl. 90
” 1 lb. ” .. .. .. ..	45kr.

“ Forty-five kreutzers, therefore, in accordance with the above, will in future be the production cost of a colour which, as is well known, could not be obtained for several hundred guldens, while in green it was not procurable at any price.”

“ I venture to hope that the foregoing communication may yet prove of some interest in chemical circles.”

Ultramarine is by far the most commonly used of the blue pigments. It is a chemical combination of silica, alumina, soda, and sulphur, but its exact chemical constitution is not known, the proportions of its ingredients varying somewhat with different makes. There are two principal varieties of ultramarine sold. One is known as sulphate ultramarine the other as soda ultramarine, from the materials used in the process of manufacture. In the first, silica, china clay, *sulphate of soda*, and coal are used; in the latter, silica, china clay, *carbonate of soda*, and sulphur are used. The sulphate ultramarine is distinguished by its very pale greenish blue colour, while the soda ultramarine is of a violet hue.

Ultramarine is distinguished from other blues by the fact that acids completely decolorise it, with the evolution of sulphuretted hydrogen and the formation of a white precipitate of sulphate.

The sulphate ultramarine is more easily decomposed by acids than the soda ultramarine, and some makes of the latter more easily than others. Alkalies and heat have no action on this pigment. Boiled in strong nitric acid, ultramarine is completely decolorised, a colourless solution being formed, and a gelatinous mass of silica being left as a residue.

It is not as a rule necessary to make an analysis of the pigment; the above tests serve to distinguish it from other pigments.

An assay of ultramarine should include the following points:—1st, colour or tint; 2nd, covering power or body; 3rd, acid resisting properties: this can be tested by making a very weak solution of sulphuric acid—about 4 oz. in 1000 oz. of water—and adding a little of this to the pigment contained in a glass, and noting how long it takes to bring about decolorisation; 4th, the power of resistance to the action of alum. When ultramarines are boiled with a solution of alum, they are more or less reddened thereby; those which are made with a large excess of silica are found

to resist this action of alum better than those containing a normal quantity of this compound. Such ultramarines are preferred by the paper maker, who uses a large quantity of alum and sulphate of alumina in the sizing of his papers, and therefore he wants an ultramarine which shall not change in shade when used for tinting alumina sized papers. This point is easily tested. A solution of alum is made, and in a little of this a small quantity of ultramarine is boiled for a few minutes, and it is noted whether any change of shade occurs. If any sample is found to change much, that sample must be rejected for paper tinting, although it may be used by the painter or the laundress.

It may be worth pointing out here that ultramarine should not be used with any other colours which have a tendency to be acid, as sooner or later the colour will be destroyed. It should also not be used with lead or copper pigments, as the sulphur it contains tends to react on those metals, forming the black sulphides, thus leading to the ultimate discoloration of the mixture.—(*Chemical Trade Journal*).

## CHAPTER IV.

**BROWNS.**

BROWN colouring matters are obtained from all three kingdoms—the animal, the vegetable, and the mineral—but in greatest abundance from the last named. The natural mineral brown pigments afford almost every variety of tint, and being largely composed of silica and metallic oxides they are remarkably permanent.

ASPHALT OR BITUMEN.—These names are applied to a variety of black or brown resinous matters found in many parts of the world in a mineralised state, though derived originally from organic sources. The “Bitumen of Judæa” is supposed to be found on and around the Dead Sea, but the bulk of the product going by that name really comes from Trinidad. All kinds of asphalt have a pungent and peculiar smell, melt at a low temperature, are very combustible, and while dissolving in turpentine, and more readily in coal tar naphtha, are insoluble in water and in alcohol. Very little asphalt is now used as a pigment, but it continues to find a limited application in varnish making, notwithstanding the tendency of varnishes containing it to suffer from minute cracks with the lapse of time.

BISTRE.—This pigment is used exclusively in water-colour painting, for which purpose it affords a fine warm yellowish tinted brown. It is of vegetable origin, being prepared from the soot which is deposited in the flues leading from fire-places which consume wood fuel. Every wood, however, does not afford an equally good sample of bistre, and beech occupies the foremost rank in this respect. The brightest

and blackest soot is selected, and after careful grinding and sifting through a very fine sieve, it is repeatedly stirred up, for several hours at a time, in a series of clean hot waters, the object of which is to dissolve out all traces of tarry and other soluble matters, which very seriously affect its permanence, being oxidised on exposure to air and light, and thus weakening the tint. The washing is therefore a matter of the very first importance. The solid pigment is allowed to settle out of each wash water, and is collected and dried, being mixed with a small proportion of gum water to give cohesion. The drying is effected in a stove room.

BONE BROWN.—This unimportant pigment is simply underdone bone black (see p. 6), and is obtained by stopping the calcination of the bones at a point which falls short of thorough charring. In consequence it contains a proportion of unaltered animal matters, which sooner or later may undergo decomposition, and prejudicially affect the painting.

CAPPAGH BROWN.—A mineral pigment which is only a variety of umber, and may best be described under that head (see p. 105).

CASSEL EARTH.—Another name for Cologne earth, *q. v.*

CHICORY BROWN.—This vegetable pigment is rich-coloured but lacks permanence. It is prepared by calcining roots, such as those of chicory, in vessels to which air is not admitted, from which then results a fine brown powder. This is boiled in water, and the solution is evaporated to dryness, yielding a brown pigment, which, being soluble in water, is sometimes employed by water-colour artists.

COLOGNE EARTH.—This material, which is also known as Cassel earth or Rubens brown, is an earthy carbonaceous substance, probably derived from the decomposition of lignite or brown coal, readily undergoing combustion without emitting flame or smoke. Large deposits of it are worked in the vicinity of Cologne, whence its name. It is blackish-brown in colour, smooth and crumbling to the touch, and very light. To remove soluble impurities it is subjected to several washings in water, and then collected, mixed with a

little gum-water, and dried in small moulds. The colour is used by artists, but is very variable in composition and uncertain in durability.

MANGANESE BROWN.—One of the most durable brown pigments used by the Romans is found to be oxide of manganese, which discovery has led to the proposal to prepare the binoxide of that metal as a brown pigment. The method suggested is as follows :—

The protochloride of manganese, derived from the manufacture of chlorine, or the protosulphate resulting from the calcination of the protoxide with iron sulphate, is dissolved in warm water ( $85^{\circ}$ – $105^{\circ}$  F.); to this is added a sodium hypochlorite solution, or a solution of potassium hypochlorite containing a small proportion of carbonate of soda, the addition being continued until the precipitated manganese binoxide ceases to change colour, marking the completion of the oxidation. The supernatant clear liquor is drawn off, and the precipitate is washed first with acidulated water (containing 2 per cent. of sulphuric acid), and then with pure water till all trace of the acid is removed. The dark-brown impalpable powder of manganese binoxide is stove dried, and forms a permanent and safe pigment with good covering power.

MARS BROWN.—One of the products obtained by the calcination of Mars yellow (*q. v.*) at various temperatures and under different conditions is a full-tinted and durable brown due to sesquioxide of iron. Another method of preparing it is from alum, sulphate of iron, and chloride of manganese. In either case the pigment is not superior to umber or oxide of iron, while it cannot be produced as cheaply.

PRUSSIAN BROWN.—An artists' colour known by this name is prepared from Prussian blue, but as it has no superiority over Vandyke brown or umber, and is higher priced, it is not in general use. It consists essentially of carbon and ferric oxide, resembles bistre in tone, and possesses durability and good covering powers. The operation of calcining the Prussian blue should be conducted slowly, and is best performed in a closed vessel, though it may also be done in the open.

The pieces of blue should not be larger than a hazel nut. They soon split, scale off, and become red, when the heating should cease. On breaking the cooled particles they will show a patchy coloration varying from yellowish-brown to black. On grinding, the mass assumes the desired brown hue.

RUBENS BROWN.—Another name for Cassel brown or Cologne earth (*q. v.*).

SEPIA.—This is one of the few pigments derived from the animal kingdom. It is produced by several sea-inhabiting creatures belonging to the class called *Cephalopoda*, and more particularly by two members of the genus *Sepia*, known respectively as *Sepia officinalis* and *Sepia loligo*. A peculiarity of these cephalopods is that they are provided with what is commonly called an ink bag, in other words a gland or sac filled with a blackish-brown liquid, which possesses intense colouring power. The object of the secretion is the protection of the creature from pursuit by its enemies, a portion of fluid being discharged at will, and so obscuring the surrounding water that escape is facilitated.

For the sake of this pigment the cuttle-fish are sought after by fishermen in the localities frequented by the animals, notably in the warm waters of the Mediterranean. When the creatures are captured, their glands are carefully extracted and sun-dried so as to solidify the contents. In this state ink bags are sent into commerce. The colourman subjects the sacs to boiling in a solution of soda or potash, whereby the colour is dissolved out of the receptacle, and being filtered clear of all fragments of the animal tissue, is next precipitated by the addition of acid, collected on a filter, washed, and dried. It then forms an exceedingly useful pigment, having, according to Prout, the following average composition :—

	Per cent.
Black pigment (melanin) about .. .. ..	78
Calcium carbonate .. .. .. ..	$10\frac{1}{2}$
Magnesium carbonate .. .. .. ..	7
Alkaline chlorides and sulphates .. .. ..	2
Organic matter .. .. .. .. ..	1

It is remarkably permanent for an organic substance, suffering no alteration on being combined with other pigments, and withstanding the effects of exposure to air and light. Though slightly transparent, and not quite constant in tint, it possesses very great colouring power. Being of extremely fine texture it can be worked up equally well as an oil colour or as a water colour, but it is especially in the latter capacity that it forms an indispensable artists' colour, and permits the production of a great range of shades and tints.

ULMIN.—The pigments grouped under this name are also of organic origin; but though they possess good colour, mix well, and flow readily from the brush, they lack the durability which is essential to their successful use. The following methods have been employed in their preparation:—(1) Fused caustic potash is digested in alcohol, and the liquor filtered and heated till a brown powder is thrown down, which is filtered and washed with acidulated water; (2) Waste cotton, peat, or brown coal, heated with an alkali; (3) Farinaceous matters carbonised by mineral acids.

UMBERS.—These form a large class of natural earths of a brown colour, differing widely in the proportions of their chief constituents, but closely allied to the ochres and siennas in general composition, and owing their colour mainly to the presence of hydrated oxides of iron and manganese, the latter prevailing in the umbers to a greater degree than in the ochres and siennas, which consequently belong to the yellow group (*q. v.*).

Beds or veins of umber of varying thickness and extent are found in many places, especially in connection with magnesian limestone (dolomite). Apparently they are often derived from decomposition of this rock, perhaps due to the infiltration of carbonated water, which has acted upon the calcium and magnesium carbonates in the dolomite, and left the silica and the iron and manganese as oxides, forming the bulk of the umber. Usually these beds of umber are near the surface, though covered by an overburden of

vegetable soil, and the operation of working them may be called quarrying rather than mining, being of a superficial and simple character, often only amounting to small pits.

As no umber is a definite body, but rather a mixture of various substances, so the composition of every kind is peculiar to itself, and very wide differences are noticeable. Even the same bed will not necessarily produce always the same class of umber. The following figures show the extent to which the proportions of the several ingredients may vary:—

	Per cent.
Water given off at 212° F. .. .. ..	4 to 65
Water in combination .. .. .. ..	5 to 11½
Silica .. .. .. .. ..	4½ to 29½
Manganese dioxide .. .. .. .. ..	7 to 27
Ferric oxide .. .. .. .. ..	6 to 36

Calcium carbonate is sometimes present to the extent of 2½ to 6 per cent., and at other times is quite absent, its place being taken by  $\frac{1}{2}$  to 1 per cent. of lime (calcium oxide); some of the English umbers contain about 2 per cent. of calcium sulphate (gypsum) in addition to the carbonate. Alumina may occur to the amount of 2½ to 12½ per cent., or may be wanting altogether. In a sample of Derbyshire umber analysed by Hurst there appears to have been over 30 per cent. of barium sulphate (barytes), which looks suspiciously like adulteration.

Almost every variety of shade may be found in umbers. The darkest and richest in colour—a warm violet-brown—is the so-called Turkey umber, mined in Cyprus, and formerly shipped via Constantinople; this is of very fine quality and commands the higher price in the market. A reddish-brown Irish umber, known as Cappagh brown, obtained from the Cappagh mines in Cork county, is much esteemed among artists, both for water-colour and oil painting, and especially for the latter when it has been subjected to a preliminary desiccation at a temperature of

about 170° F. Heated to the boiling point its colour changes to a rich red, resembling burnt sienna. Cornish umbers are of fairly good quality. Derbyshire umbers are poor, and incline to a reddish tint, besides being gritty. Sometimes they are adulterated with a little lamp black, which renders the tone more like that of Turkey umber, and thus deceives the unwary buyer.

There are three conditions in which umbers come into commerce: (1) as raw lump, being the mineral just as it is mined; (2) as raw powdered, when it has been ground very fine and levigated or washed in flowing water, whereby the particles get assorted according to their several degrees of fineness; and (3) as burnt, being the powder after it has been subjected to calcination in a closed furnace. Some umbers are so soft that they can be washed without any previous grinding, but this is not generally the case. The apparatus used in grinding and levigating is common to all pigments where these processes are employed, and will therefore be described once for all in a later chapter. The calcination is conducted at a red heat, and by this process the tint is made darker and warmer, but it must not be pushed too far or the pigment will blacken.

While different samples of umber present differences of tone and shade, from a yellowish to a violet brown, they are alike in being very durable and proof against the injurious influences of air, light, and impure atmospheres; ordinary acids and caustic soda have no appreciable effect. They mix well with other pigments without provoking any change, and are equally satisfactory as oil or water colours. They do not admit of much adulteration, except in the substitution of an inferior grade for a superior one, and possibly the addition of barytes as a make-weight.

VANDYKE BROWN.—What the original brown used so much by the great Van Dyke was no one can tell. The pigments now sold under the name of Vandyke brown are of varying composition, some being simply mixtures of red oxide of iron

and lamp black, others are natural earthy substances after the character of Cologne earth, and others again are artificial products of the partial carbonisation of vegetable matters, such as cork waste. As it is uncertain what was the composition of the original Vandyke brown, no standard of chemical purity can be established.

Probably the most general sources of Vandyke brown are red oxide and lamp black, and the quality of such a pigment will chiefly depend on securing a good black, as any traces of unburned oily matter will make the paint difficult to dry. Almost any variety of shade can be produced by adjusting the proportions of lamp black and red oxide, with sometimes the addition of a little ochre. The pigment made in this manner forms the staple brown paint for industrial application, mixing well with oil, and being of a durable character, but it does not mix so well with water.

Vandyke browns of the Cologne earth type, from earthy lignites and peaty matter, are much used in and around the localities where they are produced, and entail nothing more than grinding and levigation to fit them for the market. They are in general best adapted to water-colour painting.

Warm and slightly reddish tints of Vandyke brown are obtained by the partial carbonisation of ligneous material, in other words by subjecting cork and bark waste to moderate calcination in closed retorts. These mix equally well in water or oil.

All varieties of Vandyke brown are stable pigments, without any disturbing influence when used in admixture with other colours, and quite proof against any change on exposure to air and light. Next to the umbers they are the most generally useful browns.

## CHAPTER V.

### GREENS.

GREEN pigments form an important and numerous class, but many of those which possess the most brilliant and durable qualities contain highly poisonous ingredients, and some of the most beautiful are not permanent. All things considered they are perhaps the least satisfactory group of colouring matters. The following list comprises all worth notice.

BARYTA GREEN.—It is said that the manganate of baryta makes an excellent green pigment, which may with advantage replace for many purposes those greens which contain arsenic. Several methods of preparing it have been published:—(a) One consists in igniting together the nitrate of baryta and manganese oxide or dioxide. (b) Another consists in fusing a mixture of pyrolusite or black oxide of manganese, caustic baryta, and chlorate of potash. (c) According to a third method, mix 2 parts caustic soda and 1 part chlorate of potash, and gradually add 2 parts very finely powdered manganese; heat gradually up to dull redness, then allow to cool, powder, and exhaust with water; filter and cool, and add a solution of nitrate of baryta to the filtrate; a violet-coloured baryta precipitate forms; this is carefully washed, dried, and treated with  $\frac{1}{2}$ -1 part of caustic baryta, hydrated, and gradually heated up to redness, with constant stirring. The cooled mass is powdered, and finally washed to remove any excess of baryta.

By either process a green mass is obtained, but the second

method seems to yield a more beautiful and homogeneous product. In experimenting with other and more direct methods for preparing a baryta green of great purity and beauty, Fleicher has made several observations of its properties. If a green solution of manganate of potash be precipitated, while boiling, by chloride of barium, a heavy, granular, but not crystalline, precipitate of manganate of barium is obtained. This precipitate has a violet colour, approaching blue, can be washed by decantation at first, and afterwards may be collected on a filter. On drying the precipitate, its colour grows lighter with the increase of temperature; and on being heated to a dark red heat, it looks almost perfectly white, with only a shade of greyish blue. If, then, it be heated still higher with free access of air, or in an oxidising flame, it gradually turns green; by carrying the process farther the colour becomes a beautiful greenish-blue, and finally, at a very high heat, a dirty greyish-brown mass is formed from the reduction of the manganic acid to binoxide of manganese. On adding chloride of barium to a solution of the permanganate of potash, and boiling, a precipitate is slowly formed of a peach-blossom colour, while the liquid retains a deep violet colour. By decanting and bringing the mass, diluted with water, on a filter, the precipitate is not decomposed, and can be dried at 212° F. without changing colour. When the dry permanganate of barium is gradually heated, its colour also grows paler, but does not, like the manganate of baryta, acquire a green colour at a still higher temperature; for after the colour has once vanished, an increase of temperature soon converts it into the greyish-brown mixture of the binoxide of manganese and baryta or carbonate of baryta. Hence it is impossible to prepare the green manganate of baryta from the permanganate.

In regard to the colour itself, experiments have shown that the most beautiful green is that formed by igniting the manganate as described above. The green prepared

by Rosenstiehl's process—fusing together caustic baryta, chlorate of potash, and binoxide of manganese—is less beautiful than the above; while that attained from nitrate of baryta and binoxide of manganese is far inferior to either of the others. Perhaps, however, this colour could be improved by preparing it in a reverberatory furnace with a strong oxidising flame.

The blue-green baryta pigment has different shades, according to its preparation, some being almost pure blue with only a shade of green, and resembling the light blue quill feathers of many parrots. The greener the colour the more it gains in intensity, but it loses in fineness, although still surpassing the green manganate of baryta.

The production of the blue or bluish-green baryta is due entirely to the alkaline property of the mass. Whether each definite colour is due to a definite composition is doubtful, since the temperature, which must not exceed that of a bright red heat, exerts a greater influence on the colour. This much is however certain, that both manganic acid as well as the permanganate of baryta, when mixed with about 20 per cent. of hydrate of baryta and ignited at a red heat, will always produce this blue-green colour. It is evident that the blue-green colour is dependent entirely on its basic character; for on placing this powder in weak acids, it first turns green and is then gradually decomposed. The baryta pigment is quite permanent, and may be subjected to the action of strong sulphuric acid for hours, at the ordinary temperature, before the colour will be destroyed. Boiling potash solution has no perceptible effect upon it. The permanence, especially of the blue shade, is increased by adding a little baryta, which increases its alkalinity. It is also worthy of remark that the pigment prepared from the nitrate of baryta is much less permanent, because the nitrous acid present will after a time exert a reducing action.

The baryta pigments seem especially adapted to fresco painting, because they appear very bright and lively on

stone, and especially on lime, where many other pigments lose their beauty or are entirely destroyed.

BREMEN GREEN.—This old-fashioned pigment is a basic carbonate of copper, and has been produced in several ways. At first a basic chloride or oxychloride was used, its mode of preparation varying somewhat but without affecting the character of the result, the great essential being that no subchloride of copper should be present. Therefore, in some factories, it was the practice to prepare the magma of basic oxychloride even a year in advance; or, to subject it to repeated wetting and drying in order to ensure perfect oxidation. The method has now become obsolete, and is superseded by the following:—

When neutral nitrate of copper is decomposed by an insufficiency of a potash carbonate solution, the flocculent precipitate of copper carbonate formed at first is gradually changed into a subnitrate of copper which is precipitated as a heavy green powder. In practice the operation is conducted as follows:—Copper scales are calcined in a reverberatory or muffle furnace, till all the suboxide is converted into protoxide, or until a sample dissolves in nitric acid without evolution of red nitrous vapours. The copper nitrate solution is heated and decomposed by a clear solution of potash carbonate, and when the effervescence subsides, small doses of potash carbonate solution are added, till but little undecomposed copper remains in the solution. To recover this last portion, the clear liquor is decanted, and the green precipitate is washed several times with small quantities of water. All the liquors are collected, and the remaining copper is precipitated by potash solution. The green carbonate of copper is introduced into a new solution of copper nitrate, in which it is transformed into a basic salt. The previous liquors are evaporated till they afford crystals of nitrate of potash, which is a valuable secondary product.

BRIGHTON GREEN.—The following recipe has been pub-

lished for making this pigment. Dissolve separately 7 lb. sulphate of copper and 3 lb. sugar of lead, each in 5 pints of water; mix the solutions, stir in 24 lb. of whiting, and when the mass is dry grind to powder.

BRUNSWICK GREEN.—(a) Old process.

The Brunswick green of former days was closely allied to Bremen green, essentially consisting of a basic chloride or oxychloride of copper, and possessing all the faults incidental to that class of copper salt. While having fairly good covering power, and capable of being used either as a water colour or an oil colour, it was tedious and therefore expensive to prepare, and not thoroughly durable under exposure to air and sunlight. Nevertheless it was a useful bluish-green pigment. Following are some of the many methods by which it has been prepared :—

(1) Poor oxidised copper ores are moistened with hydrochloric acid, and spread out exposed to the air. The metal is thus rendered very susceptible to the action of chlorine, and is even attacked by solutions of ammonium chloride and of common salt. The sub-chloride produced is rapidly transformed into oxy-chloride, and forms a fine light-green pigment.

(2) Place 2 parts by weight of copper filings in a vessel capable of being tightly closed, and over them pour 3 parts by weight of salammoniac in the form of a saturated aqueous solution. Keep the mixture in a warm place for some weeks and thoroughly agitate it occasionally. In due time the newly formed oxychloride is removed from the vessel, and separated from the non-oxidised copper by washing on a sieve. This washing must be continued until all traces of alkali have been destroyed, when the pigment is drained, and very slowly dried at a low temperature to avoid decomposition.

(3) Copper scrap is covered with a concentrated solution of chloride of copper and allowed to remain until the chloride has undergone conversion into basic chloride. The

latter is then subjected to the straining, washing, and drying treatment prescribed in (2).

(4) In a lead-lined vessel, place a quantity of copper filings or waste, and add to it two-thirds of its weight of common salt, and one-third of its weight of concentrated sulphuric acid, the latter being however first diluted by admixture with three times its volume of water. The mass is left to stand, with occasional stirring till all the copper has been transformed into oxychloride, when it is strained, washed, and dried as in (2).

(5) A modification of (4) is to put the copper scrap into a wooden vessel, and cover it with an equal weight of common salt and an equal weight of sulphate of potash dissolved in water. After standing and agitation as before, the oxychloride is formed, and the straining, washing, and drying are repeated.

(6) A solution of crude carbonate of ammonia is added to a mixed solution of alum and blue vitriol so long as any reaction takes place. When it is completed, the precipitate is collected, washed, and dried as in the other cases.

(7) Lighter shades are produced by the addition of alum, or of sulphate of baryta.

(b) New process.

The modern Brunswick greens, which are made in a variety of shades, and sometimes known as chrome greens, Prussian greens, Victoria greens, and by other fancy names, really consist of a white pigment as a basis—usually sulphate of baryta (barytes), but occasionally also sulphate of lime (gypsum) and sulphate of lead—coloured green of varying intensity and depth by addition of a blue pigment in the shape of Prussian blue, and a yellow in the guise of chrome-yellow. There are what may be called four distinct standard shades recognised by colour-makers, viz. “pale,” “medium,” “deep,” and “extra deep”; but inasmuch as every manufacturer adopts a formula of his own, there may be appreciable differences among colours of the same nominal standard if by

different makers. Taken as a whole, about three-fourths of their total weight consists of the foundation white pigment, usually barytes; about 1 to 6 per cent. is Prussian blue, according to the shade; and 14 to 18 per cent. chrome yellow; but there are brands occasionally met with which depart considerably from these average figures.

The actual ingredients employed to form these green pigments are essentially different, according as the wet or the dry method of combining them be adopted. In selecting the various ingredients the following points must be borne in mind. The Prussian blue of every maker is not the same in quality, and while the character of the blue is not of the foremost importance when dark greens are being made, for light shades of green, on the other hand, it is essential to select only the best and brightest brands. In the same way the tint and quality of the chrome yellow are liable to considerable fluctuation, and it is almost impossible to ensure two lots having exactly the same characteristics, consequently the only way in which a certain shade of green can be ensured is by experimental trial with small quantities for each batch. Middle chromes can be used for deep greens, but only the lemon chromes for pale shades. Regarding the barytes which forms the basis of the pigment, there are no special precautions to be observed; and the same may be said of the gypsum, should that be adopted as a substitute for the barytes, except that 1 part by weight of gypsum takes the place of about  $2\frac{1}{2}$  parts of barytes. The latter, however, is much the more commonly used. For the dry method of compounding Brunswick greens, the above named ingredients are all that are required.

In the wet method there is this essential difference, that it is sought to precipitate the blue and yellow colours upon the inert base by bringing about certain reactions, and therefore while the base remains the same as in the dry method, the colouring media are totally distinct, consisting of lead acetate, bichromate of potash, sulphate of iron, and yellow or

red prussiate of potash. The chief condition to be observed with regard to the lead acetate is that it shall be in the proportion of slightly more than three to one of the bichromate of potash ; in other words, the bichromate should be a trifle less than one-third the weight of the lead acetate. As to the iron salt, if commercial acetate or nitrate of iron could be bought of constant quality or purity, that would be the most convenient form ; but failing that, recourse is had to freshly made and good quality sulphate of iron (green copperas). It is found that the best results are secured when the weight of the sulphate of iron is exactly the same as that of the prussiate of potash. On the score of economy, the yellow prussiate of potash (ferrocyanide) is employed, but the red prussiate (ferricyanide of potassium) gives better and more certain results, and should be adopted when making a superior paint which will command a higher price.

As to the comparative merits of the wet and dry systems of mixing the ingredients of Brunswick greens, preference must be given to the former on the score of quality of the pigment produced, but on the other hand it entails much more trouble and skill, and there never can be the same degree of control over the conduct of the operation or the shade of colour developed. The dry method, however, though much more easily carried out, and enabling the exact shade desired to be obtained to a nicety by adding a little more of either the blue or the yellow during the process of manufacture, is seldom adopted, because the quality and fineness of the tints thus secured are much inferior.

The modus operandi with the wet method is as follows :— The barytes, in the requisite fine state of subdivision, is very thoroughly stirred up with water in a capacious vessel fitted with an agitator, the water being in sufficient quantity to make quite a fluid mass. In convenient proximity to the barytes tank, and elevated above it, provide three other tanks of lesser capacity furnished with means of discharging their contents into the barytes tank. In one of these smaller tanks dissolve the green copperas in cold water ; in another,

the sugar of lead; and in the third the bichromate and prussiate of potash together. When all the salts are thoroughly dissolved, and while the barytes is kept in constant agitation, admit first of all the copperas solution, then the lead acetate solution, and finally the combined bichromate and prussiate solution, never allowing the stirring to slacken till after the last drop of these solutions has been introduced. When the commingling of all the ingredients is judged to be complete, the green pigment formed is allowed to subside, and the clear supernatant fluid is siphoned off. The pigment is washed several times by admitting clean water, agitating and settling, and finally is removed, drained on a filter, and slowly and carefully dried. Many ways of arranging the apparatus will suggest themselves, the chief point to keep in mind being to economise labour as much as possible.

The dry method of mixing is simplicity itself in comparison with the above, and merely entails putting the component materials—barytes, chrome-yellow and Prussian blue—through an edge-runner mill simultaneously, in the proportions adapted for producing the shade required.

In giving formulæ for compounding these Brunswick greens, it must be understood that they are not absolute, as every manufacturer adopts his own particular proportions for a certain shade, but they form a sufficiently approximate basis from which to work. They are all computed for 100 lb. of barytes forming the body of the new pigment:—

*Pale*: Wet—1 lb. each copperas and prussiate, 12 lb. lead acetate,  $3\frac{3}{4}$  lb. bichromate.

Dry—80 lb. chrome yellow,  $1\frac{1}{4}$  lb. Prussian blue.

*Medium*: Wet— $1\frac{1}{2}$  lb. each copperas and prussiate,  $12\frac{1}{2}$  lb. lead acetate, 4 lb. bichromate.

Dry—30 lb. chrome yellow,  $2\frac{1}{4}$  lb. Prussian blue.

*Deep*: Wet—2 lb. each copperas and prussiate, 13 lb. lead acetate,  $4\frac{1}{4}$  lb. bichromate.

Dry—30 lb. chrome yellow,  $4\frac{1}{2}$  lb. Prussian blue.

*Extra deep*: Wet— $3\frac{1}{2}$  lb. each copperas and prussiate,  $14\frac{1}{2}$  lb. lead acetate,  $4\frac{1}{2}$  lb. bichromate.

Dry—30 lb. chrome yellow, 7 lb. Prussian blue.

The Brunswick greens are in the front rank of green pigments so far as covering power is concerned, and, when made from reliable materials, are reasonably durable under the influence of air and light, in which respect, however, they vary considerably. They can be used as water colours, but are superior in oil paints. Precautions are necessary in mixing them with other pigments. By the action of sulphurated hydrogen, or sulphur in any form, the colour is darkened to a notable degree; by the action of acids, the chrome is destroyed and the green becomes blue; by the action of alkalies, both the blue and the yellow constituents are affected, and the green gives place to a reddish hue. The pale and medium shades are yellow greens; the deep and extra deep are blue greens.

These colours can be distinguished by heating them with caustic soda, which turns them brownish in tone, owing to the destruction of the Prussian blue. If the residue be filtered, and to the filtrate some acid and ferric chloride be added, a blue precipitate will be obtained, indicative of the presence of Prussian blue. On washing the residue with water and treating with hydrochloric acid, the brown colour disappears, and, in most cases, only a white residue of barytes is left; sometimes the residue may have a faint yellowish colour. The solution in hydrochloric acid will give the characteristic tests for iron. The yellow element can be recognised by boiling in hydrochloric acid, filtering, and allowing the filtrate to cool, when crystals of lead chloride will deposit; these, separated out and dissolved in boiling water, will give the characteristic tests for lead, such as a white precipitate with sulphuric acid, and yellow precipitate with bichromate of potash. The filtrate will have a green colour, indicative of chromium.

CHINESE GREEN.—Another name for the vegetable pigment known in China as Lokao (q.v.)

CHROME GREEN.—This name is often applied to any green in which chrome enters as an element, but more particularly

to the modern Brunswick greens described on pp. 114–118; and to the green which bears the name of its first maker, Guignet, and described under the title of Guignet's Green, see p. 125.

**COBALT GREEN.**—This remarkably stable, but somewhat costly, pigment is also known by the names of Rinmann green and zinc green, the former after the name of the chemist who first prepared it, and the latter because it contains a large proportion of zinc. It is in fact a combination of the oxides of cobalt and zinc, and was originally produced in the following manner:— $\frac{1}{2}$  lb. pure cobalt ore was dissolved in 4 lb. concentrated nitric acid, and added to a solution of 1 lb. zinc in 5 lb. nitric acid; the mixture was diluted with water, and a solution of potash carbonate was added, throwing down a pinkish precipitate, which was washed on a filter, dried, and calcined at a high temperature.

Wagner found that an indispensable condition was to have a protoxide of cobalt as free as possible from foreign metals, with which object he practised the following method:— Cobalt oxide is dissolved in three equivalents of hydrochloric acid, and the solution is evaporated to dryness; the residue is dissolved in six equivalents of water, and through the solution is passed a current of sulphuretted hydrogen gas, so long as any precipitate is formed. This precipitate consists of sulphides of the foreign metals. The clear solution is siphoned off, evaporated to dryness, and the residue is dissolved in water. As required, this solution is treated with carbonate of soda, and the precipitate, washed, and while still wet, is mixed with zinc white. The reddish mass produced in this way is dried and calcined. The best tone is attained by combining 9 to 10 parts of zinc oxide with 1 to  $1\frac{1}{2}$  parts of cobalt protoxide.

Louyet has shown that if the cobaltic solution be precipitated by the phosphate or the arseniate of potash, the corresponding salt of cobalt thus produced possesses the property of imparting a green colour to zinc white at a

much lower temperature than is required in the case of ordinary protoxide of cobalt: moreover, the pigment gains in body, and the colour gains in purity and brightness. If a small quantity of arsenious acid is added to the ordinary mixture before calcination, the calcined mass will assume a remarkably bright green colour; and its structure being loosened by the disengagement of fumes of arsenious acid, it will be easy to grind.

According to Barruel and Leclaire's method, 1 lb. of pure dry sulphate of cobalt, dissolved in hot water, is mixed with 5 lb. of zinc oxide. The mixture is dried, and calcined for three hours at a clear red heat in a muffle; when cooled, it is thrown into water, washed, and dried.

The composition of cobalt green has been shown by Wagner to vary considerably, as is to be expected from the methods of its preparation. The proportion of zinc oxide ranges from  $71\frac{1}{2}$  to 88 per cent., and the cobalt protoxide from  $11\frac{1}{2}$  to 19 per cent.; in addition, there will be fluctuating percentages of phosphoric acid, soda, oxide of iron, &c., according to the process followed.

With the single exception of its costliness, cobalt green possesses advantages over most other green pigments. It has a bright colour, sometimes inclining to a yellowish tint, or, when phosphates are used in its preparation, leaning to a blue shade. But it is always permanent, not only under the influence of air and light, but also in the presence of alkalies and any but concentrated acids; thus it may safely be compounded with other pigments.

**DOUGLAS GREEN.**—This pigment, which is fairly permanent, and possessed of considerable covering power, owes its name to the chemist who proposes its use, and its colour to the oxide of chromium. The method by which it is prepared is as follows:—Solutions of barium chloride and potassium chromate are mixed together. To the barium chromate thus produced is added one-fifth of its weight of concentrated sulphuric acid, whereby partial decomposition

is brought about, resulting in a mixture of barium chromate, barium sulphate, and chromic acid. This mixture is dried, and calcined in a crucible at bright red heat, the effect of which is that the chromic acid is converted into green oxide of chromium, and, being scattered throughout the mass, imbues it with a green colour.

EMERALD GREEN.—This is quite an old-fashioned pigment, having been in use some 80 years. It is a combination of acetate and arsenite of copper, and varies in tint from a dark to a pale green, always with a bluish cast. It possesses good covering power, and can be used either as an oil- or as a water-colour, but particularly as the latter, and is much used in paper staining. In composition it varies considerably; as there are some half-dozen industrial methods of making it; but in general terms it usually contains over 50 per cent. of arsenious acid, and about 30 per cent. of oxide of copper, together with various impurities. Following are some of the processes by which it is manufactured.

(1) According to the method introduced by Liebig, 1 part of verdigris is heated in a copper kettle with sufficient distilled vinegar to effect its solution, and to this is added a solution of 1 part of arsenious acid in water. The result is a precipitate of a dirty green colour, which is dissolved in a new quantity of vinegar and boiled for some time. In this way is obtained a new precipitate, granular and crystalline, and exhibiting a splendid green colour. When this has been filtered off, washed, and drained, it is boiled with one-tenth of its weight of commercial potash, in order to deepen and brighten the colour and destroy the bluish tint. Should the waste liquor obtained after the filtration of the pigment from the second boiling in vinegar contain any remaining copper, arsenious acid is added; and if arsenious acid be present, copper acetate is added; while if acetic acid survives it may be used again for dissolving another lot of verdigris.

(2) Form a paste with 1 part verdigris in sufficient

boiling water, pass it through a sieve to remove lumps, and gradually add it to a boiling solution of 1 part arsenious acid in 10 parts water, the mixture being constantly stirred until the precipitate becomes a heavy granular powder, when it is filtered through calico, and dried very carefully.

(3) Acetate of copper is mixed with a sufficient quantity of water heated to 122° F., to make a homogeneous and liquid paste. To 10 parts of acetate of copper in this condition is added a solution of 8 parts of arsenious acid in 100 parts of boiling water, the whole being then kept in a state of ebullition. The addition of a little acetic acid helps to develop the beauty of the colour. When precipitation is complete, the clear liquor is drawn off, and forms a convenient solvent for the next charge of arsenic, the operation being facilitated by adding a little carbonate of potash, forming an arsenite of potash. The precipitate constituting the desired green pigment is filtered off and dried at the lowest effective temperature.

(4) Dissolve 5 lb. of sulphate of copper in water, and add to it a solution of 1 lb. of lime in 2 gallons of vinegar. Mix 5 lb. of white arsenic with sufficient water to form a paste. Add the arsenic paste to the copper and lime mixture, and leave the whole at rest in a moderate degree of heat. Mutual decomposition slowly ensues, with consequent formation of the green pigment, which is filtered off, washed, and dried with the same precaution as before.

When sulphate of copper is used in the production of emerald green, it is very desirable that it shall be free from sulphate of iron, which is a common impurity in the commercial article, and greatly detracts from the purity and brilliance of the pigment. A good method of eliminating this iron is to add to the sulphate of copper solution a small quantity of a gelatinous precipitate of carbonate of copper, produced by decomposing a copper sulphate solution by a soda carbonate solution, and washing. On adding the gelatinous carbonate of copper, with agitation, the iron is

soon thrown down in flakes of oxide, and pure sulphate of copper may be filtered off.

(5) Braconnot proceeds as follows:—A solution of 3 lb. of sulphate of copper is made in a small quantity of hot water; and a second solution of 3 lb. of arsenious acid and 4 lb. of commercial carbonate of potash in boiling water. When the evolution of carbonic acid gas has ceased, the two liquors are mixed together while being kept continuously stirred; the result is an abundant precipitate of a dirty yellowish-green colour. On adding a slight excess of acetic acid, a fine crystalline green is developed; this is washed with boiling water on a filter, and dried very slowly and carefully.

(6) A rough and ready process is to mix white arsenic with water, and then stir in an equal weight of verdigris, allowing the mixture to be at rest for a time in a moderately warm temperature till the pigment is completely precipitated, when it is washed on a filter, and dried very gradually.

(7) A method due to Köchlin is described in the following terms:—An aqueous solution of sulphate of copper is made by adding 100 grammes of the salt to 500 cc. of water. To this, when solution is complete, is added  $187\frac{1}{2}$  cc. of a solution of arsenite of soda, which is of the strength represented by 500 grammes of arsenite in 1 litre of water. The result is that a precipitate of arsenite of copper is thrown down. This precipitate is treated with 62 cc. of acetic acid at  $11^{\circ}$  to  $12^{\circ}$  Tw., or half that quantity of pure formic acid, for one hour, at a temperature ranging from  $104^{\circ}$  to  $122^{\circ}$  F. The pigment thus produced is of good colour, but its superiority would not seem to justify the use of such an expensive article as pure formic acid, nor the minute adjustment of the proportions of the ingredients, in an operation to be conducted on a commercial scale.

(8) Another complicated process has been invented by Prof. Galloway, which, under skilled supervision, and when

the correct proportions of the several ingredients have been ascertained by careful experiment, may give good results, but several precautions have to be observed which cannot be entrusted to ordinary factory hands. The principle of the process is that when a quantity of sulphate of copper is dissolved in water, sufficient carbonate of soda is added to throw down one-fourth of that copper sulphate as carbonate of copper, and then so much acetic acid is introduced as will convert that copper carbonate into acetate. In order to convert the balance of the copper sulphate into arsenite, a solution of arsenic in boiling carbonate of soda is made and added to the copper acetate solution, both solutions being at a boiling temperature.

Emerald green is a pigment which possesses considerable stability in dry pure air, but in damp atmospheres it becomes brown; in the presence of acid or ammoniacal vapours it turns blue, and under the influence of sulphuretted hydrogen it blackens; moreover, strong alkalies destroy it. Consequently it cannot be used in many situations, nor in association with such pigments as contain sulphur compounds. In decorative painting it is difficult to apply on large flat surfaces, and necessitates stippling in order to get it to lie well; but when stippled on a ground of proper green it develops an exceedingly beautiful bloom-like appearance.

Its peculiar shade distinguishes it from all other green pigments, none of which approaches it in the paleness and brightness of its colour. It can be distinguished by the fact that it is soluble in acids and ammonia, to a blue solution which does not change on boiling. In caustic soda it also dissolves with a blue colour: on boiling, a red precipitate of cuprous oxide falls down. No other green pigment answers to all these tests.

There are a good many imitation emerald greens on the market, some of which are offered as genuine emerald greens, others as "emerald tint" green, which is much more honest.

The composition of these greens necessarily varies greatly, some are prepared from coal tar greens, others by careful admixture of various green, blue, and yellow pigments. If the tint of these substitutes is right and they are sold for what they are, there is no reason why they should not be used in place of the real article, over which they have the advantage of not being poisonous, which is a great disadvantage of the genuine emerald green. Although one authority disputes this point, certainly the poisonous action of emerald green varies very considerably with different individuals. The genuine emerald green may be distinguished from the spurious by being perfectly soluble in acids and alkalies, which the imitations are not; the character of the latter must be inferred by the application of a few special tests, the nature of which will be readily deduced from what is said as to the properties of other green pigments. Emerald green should be assayed for purity and tint; this is important, as pure emerald green has a tint of its own, which is difficult to imitate, and sometimes really pure emerald green offered for sale is of a defective tint, due to some fault in the process of manufacture. Such samples should be rejected.

**GUIGNET'S GREEN.**—The greens of this class, which owe their colour to chromium oxide, are also known as "chrome greens," a name which they share with a totally different group into whose composition chrome yellow enters as a constituent, and which have been already described under the synonym "Brunswick greens," on pp. 114-118.

Though one of the simplest of chemical products, a great many ways of preparing chromium oxides have been proposed. One of the earliest for industrial application was that of Guignet, who has given his name to the pigment, and this may fitly commence the long list.

(1) The first method adopted by Guignet consisted in mixing bichromate of potash with three times its weight of boracic acid and moistening the mass with just sufficient

water to form it into a thick paste. This paste is put on the hearth of a reverberatory furnace, which is carefully heated to a point never exceeding a dark red heat; if this precaution is neglected, the mass, instead of becoming porous, will fuse entirely, and the anhydrous oxide will be produced, which has a pale-green colour. The heated paste, while still red hot, is thrown into cold water and washed with boiling water, in order to remove borate of potash in solution; and this solution, when boiled down and treated with hydrochloric acid, can be made to yield up most of the boracic acid it contains. The filtered and washed residue is the hydrated oxide of chromium.

(2) A modification of (1), followed by Guignet, was to replace the bichromate of potash by chromate of soda, prepared by dissolving in boiling water 61 parts of neutral chromate of potash and 53 parts of nitrate of soda. For the neutral chromate of potash, also, may be substituted a mixture of 92 parts of bichromate of potash and 89 parts of crystallised carbonate of soda, the nitrate of soda remaining as before. On cooling, in either case, the solution deposits much nitrate of potash, which is commercially valuable. The chromate of soda present in the mother liquors is obtained by evaporating to dryness. The pigment produced by the chromate of soda process is lighter in colour than that obtained with bichromate of potash. It may be still further paled by adding a little alumina, baryta, or other white pigment to the bichromate and boracic acid mixture before calcining.

(3) Equal quantities of potash bichromate and potato starch are thoroughly mixed and then calcined in a crucible at a high temperature. The product is washed with boiling water, to remove the potash carbonate formed, and any remaining undecomposed bichromate. The precipitated chromium oxide is filtered, dried, and again calcined to drive off the water. The final result is a handsome pigment which flows well from the brush.

(4) On heating in a crucible a mixture of 3 parts of neutral chromate of potash with 2 parts of salammoniac, the two salts are decomposed, the result being formation of chromium oxide mixed with potassium chloride, which latter is removed by several washings with hot water. The brilliancy of the chromium oxide is enhanced by calcination at a dull red heat.

(5) Fuse together 3 parts of boracic acid and 1 part of potash bichromate at a dull red heat on the hearth of a reverberatory furnace. Thus is formed a borate of chromium and potash, with evolution of oxygen. The mass is repeatedly washed with boiling water, which causes decomposition, and consequent separation of hydrated oxide of chromium, and a soluble borate of potash. The chromium oxide is washed, and ground very fine.

(6) When a solution of potash bichromate is poured into a neutral solution of mercury proto-nitrate, it forms an orange-coloured precipitate, which is washed and gently dried, then powdered, and heated in a stoneware retort provided with an arm dipping into cold water, by which the mercury is distilled and condensed. The residue in the retort is a highly comminuted chromium oxide, of a fine dark-green colour.

(7) On calcining potash bichromate in a crucible at a very high temperature, it is decomposed, and results in chromium oxide and potash, the latter of which can be washed out. The chromium oxide thus obtained is very dense and of a dark-green colour resembling (6).

(8) Equal quantities of flowers of sulphur and bichromate of potash are thoroughly mixed, and heated to redness in a crucible, producing a mixture of oxide of chromium with sulphide and sulphate of potash. The latter are dissolved out by washing repeatedly with hot water, leaving the chromium oxide as a finely comminuted dense powder of an intense green colour.

(9) A modification of (8) consists in adding small suc-

cessive quantities of flowers of sulphur to a boiling concentrated solution of potash bichromate. From this results a gelatinous oxide of chromium, which is washed with boiling water, dried, and calcined in a crucible at a red heat.

(10) Hydrochloric acid decomposes bichromate of potash, forming a soluble chloride of potash which can be removed by washing, and a residue of chromium oxide, which is washed on a filter and dried.

There remain for description two or three processes in which phosphoric acid plays a part, but the greens made by these methods do not possess the freshness of the others, and it is difficult to see what advantages can attend this modification.

(11) According to Arnaudon, 149 parts of bichromate of potash are thoroughly incorporated with 128 parts of crystallised neutral phosphate of ammonia, and the mixture is heated in thin layers to a temperature between 338° and 356° F., which brings about intumescence, change of colour, and disengagement of water and ammonia; the heating is continued for half an hour, but must not be allowed to exceed 392° F. When the development of the green colour is complete, the product is washed with hot water to remove soluble salts, and the residue constitutes an impalpable powder of chromium oxide, forming a leaf-green pigment.

(12) Dissolve 10 lb. of bichromate of potash and 18 lb. of phosphate of soda in boiling water, and add to the boiling mixture 10 lb. of thio-sulphate of soda solution and a little hydrochloric acid. A precipitate of phosphate of chromium is gradually thrown down as the boiling is maintained.

For general utility no class of pigments can exceed the several forms of Guignet's green. It is capable of affording a great variety of tints, all absolutely permanent under reasonable conditions. No ordinary agent will decompose them, and they will stand almost any test to which they

may be subjected without losing colour. They are quite insoluble in acids and alkalies, and are not affected even by the extreme heat of the glass furnace. They possess good covering power, do not suffer in brightness or purity under artificial light, and are equally useful as oil or water colours, besides being admirably adapted for fresco and silicious painting, and employed in making green glass and in calico printing. They can be mixed with any other pigment. Adulteration with Brunswick or Prussian greens is often practised, but may be discovered by a portion being dissolved on boiling with caustic soda, the solution giving a precipitate of chrome yellow on adding acetic acid, and (a separate portion, of course) Prussian blue with hydrochloric acid and perchloride of iron.

LOKAO.—This pigment, which is also known as “Chinese green,” was first met with as a sediment left after dyeing cotton cloths with the barks of one or more species of buckthorn, notably *Rhamnus chlorophorus* and *R. utilis*, and passing in China under the general name of Lo-Kao. This sediment is spread on blotting paper and thus dried, forming thin cakes. Latterly, the juice afforded by the berries of the same trees is extracted by pressure, absorbed by alum, and dried in the same form of little cakes. When first introduced into England it was highly valued as affording a pure green, even in artificial light. Its price on the London market in 1861 was 7s. 6d. an ounce. So long ago as 1853 it was imported into France and used for dyeing silk. The colouring principle appears to consist of a glucose (lokaose) and an acid (lokaonic acid). In 1864, Chauvin obtained an identical colouring matter from *Rhamnus catharticus*, or the common buckthorn, a shrub which grows wild in most parts of Europe, and found a ready market for the pigment at 37s. a pound. This was simply the article known as sap green (see p. 132.)

MALACHITE.—This is one of the names applied to mountain green (q.v.).

MANGANESE GREEN.—Several formulæ have been published for making a green pigment from manganese, as follows :—

(1) An intimate mixture of 80 parts of nitrate of barium, 14 parts of oxide of manganese and 6 parts of sulphate of barium, is placed in a crucible and heated to bright redness until the green colour is thoroughly developed. The fused green mass is poured out of the crucible, cooled, and ground wet to a fine condition.

(2) To 3 or 4 parts of caustic baryta moistened with water are added 2 parts of nitrate of barium and 2 parts of oxide of manganese ; the whole mass is most intimately mixed, then put into a crucible in a furnace, and subjected to a dull red heat so long as may be necessary for securing complete decomposition. When the green colour is satisfactorily produced, the mass in a state of fusion is poured out, cooled, pulverised, digested in boiling water, then washed with cold water, and finally dried in an atmosphere which is free from carbonic acid.

(3) The oxide of manganese may be replaced by the nitrate, when the quantities are 46 parts nitrate of barium, 30 parts of sulphate of barium, and 24 parts of nitrate of manganese ; the fusion, grinding and washing are repeated as before.

According to some recipes the powdery pigment, consisting essentially of manganate of barium, is mixed with a little dextrine to make sure of its stability, but it is not clear whether this is really essential.

MINERAL GREEN.—This is only another name for the green made from copper carbonate, and described under mountain green, see p. 131.

MITIS GREEN.—This pigment is an arseniate of copper, and bears a very close relationship to the emerald green made according to Braconnot's formula, and described in the fifth paragraph of that section, see p. 123. Mitis green is prepared by dissolving arseniate of potash in five times the quantity of hot water and adding a solution of an equal

weight of sulphate of copper, keeping the whole in constant agitation. A pulverulent precipitate is formed, possessing a grass green colour. This is washed and dried. The tint can be varied by altering the proportions of the arseniate and sulphate. The arseniate of potash is made by boiling arsenious acid in concentrated nitric acid, filtering, and saturating with carbonate of potash. The arseniate is allowed to crystallise out of the liquor.

MOUNTAIN GREEN.—This pigment is also known by the names of malachite and mineral green.

(1) In its native form the mineral malachite or green carbonate of copper is very widely distributed in Europe, Asia, America, and Australia, but on a commercial scale it is chiefly produced in the Ural mountains of Siberia and in the Banat of Hungary. It only needs to be picked clean from adhering rock and to be ground to a very fine powder in order to render it ready for use. It is much superior to any of the artificial substitutes referred to below, but its cost confines its application to artistic work.

(2) Sometimes a little orpiment or chrome yellow is ground up with the malachite.

(3) A very simple formula for making the artificial pigment is to add solution of carbonate of soda or potash to a hot mixed solution of alum and bluestone (sulphate of copper).

(4) Other recipes for making mountain greens have been published which bear no relation to the composition of the original article, *e.g.* by mixing a solution containing potash and arsenic with a solution of bluestone; or, as a much more complicated example, treating a solution of bluestone first with slaked lime, then with a solution of arsenic and soda obtained by boiling in water, and finally with tartaric acid.

The advantages attendant on so much trouble in producing what is at best an unstable pigment are not very apparent.

PARIS GREEN.—This is another name, used especially in America, for the emerald greens described on p. 121.

PRUSSIAN GREEN.—A name often applied to class *b* of the Brunswick greens (see p. 114), or in other words, those which are prepared from Prussian blue.

RINMANN GREEN.—The first cobalt green (see p. 119), put on the market was made by Rinmann, and hence it is still often called by his name.

SAP GREEN.—This vegetable pigment or lake is closely allied to the Chinese green or lokao, described on p. 129.

It consists of the solidified juice extracted from the berries of the common buckthorn shrub (*Rhamnus catharticus*), which is obtained either by allowing the berries to undergo slight fermentation for about a week in wooden tubs, then pressing and straining; or by boiling the berries, and straining off the juice. In either case the clean juice is boiled down to a syrupy consistence, and a little alum (about  $\frac{1}{2}$  oz. to the pint of thickened juice) is added, the liquor being then evaporated to dryness, or very nearly to that point, the drying being left to complete itself after the pigment has been run into bladders.

The quality of this green is liable to serious fluctuation, owing to the neglect or ignorance of certain simple precautions. Thus, for a true green the berries should be selected before they have quite reached maturity. The more nearly ripe the berries are, the more yellow will be the tint of the green afforded by them. The boiling of the berries, if followed, and the evaporation of the juice, must be done at a low temperature, and the final stages of the evaporation cannot safely be done with direct fire heat, but should be effected in a water bath. The only substance incorporated with the juice should be potash alum. Sometimes it is replaced by carbonate of magnesia (which destroys the transparency of the pigment); or by carbonate of potash (which introduces a stickiness or viscosity).

Sap green possesses too little body and is too translucent for

use as an oil paint; but being non-poisonous, and in fact perfectly harmless, it finds many useful applications outside of water colour and pastel painting, viz. in colouring alimentary substances such as drinks and sweets. Its true colour is a leaf green, glossy and translucent. In durability it is not remarkable.

**SCHEELE'S GREEN.**—For more than a century has Scheele's green been a familiar pigment, but the reputation it enjoyed in its early days has long since departed, and it is now to be classed among the inferior green colouring matters. It consists essentially of a basic arsenite of copper, and contains from 8 to more than 40 per cent. of arsenic, according to the mode of preparation, of which there are several, as follows:—

(1) A mixture of 2 parts of commercial carbonate of potash and 1 part of powdered arsenious acid (white arsenic), are dissolved in 35 parts of boiling water; the solution is filtered clear, and then added gradually and while still warm to a filtered solution of 2 parts of sulphate of copper until no further precipitate goes down. This latter is collected, washed with warm water on a filter, and slowly dried without excess of heat.

(2) The preceding formula is modified by making one solution of the arsenic and the sulphate of copper, and precipitating by adding the carbonate of potash solution till the colour is fully developed, agitation being constantly maintained.

(3) Another variation is to mix the arsenic with soda crystals in boiling water, and to pour the arsenite of soda solution thus formed into the bluestone solution, the boiling being kept up for a few minutes.

Scheele's green has a pale yellowish cast, and mixes well with either water or oil, but it lacks brightness, durability, and covering power, in addition to being highly poisonous, and though once much employed in staining wall papers, is now generally discarded.

SCHWEINFURTH GREEN.—This is an old-fashioned name for emerald green, which has been described on pp. 121–125.

TERRE VERTE.—Rendered into English, the name *terre verte* means “green earth.” It is applied to a number of green-coloured earths found widely distributed in rocks of various ages, but especially in those of a basaltic or porphyritic character. In commercial quantity it occurs notably in Cyprus and near Verona in Italy; the latter locality is so important that the pigment is often known as “Verona earth.”

Notwithstanding minor points of dissimilarity in samples from different sources, there is a great family likeness among them, sufficient to indicate that the essential constituent is a silicate of iron and magnesia. The other ingredients vary with the locality producing the mineral. The same may be said of the physical characteristics, some specimens being soft and earthy, while others are hard and glassy. All possess the peculiar soapy touch of the magnesian earths, and a clay-like odour. Analysis of a Verona earth gave:—

	Per cent.
Silica .. .. .. .. .. .. .. ..	51·21
Iron protoxide .. .. .. .. .. .. ..	20·72
Magnesia .. .. .. .. .. .. .. ..	6·16
Water .. .. .. .. .. .. .. ..	4·49
Alumina .. .. .. .. .. .. .. ..	7·25
Soda .. .. .. .. .. .. .. ..	6·21
Manganese protoxide .. .. .. .. .. .. ..	trace.

While a Cyprus earth showed:—

	Per cent.
Silica .. .. .. .. .. .. .. ..	51·5
Iron protoxide .. .. .. .. .. .. ..	20·5
Magnesia .. .. .. .. .. .. .. ..	1·5
Water .. .. .. .. .. .. .. ..	8·0
Potash .. .. .. .. .. .. .. ..	18·0

The presence of copper would point suspiciously to adulteration, and in any case should suffice to condemn the sample for use.

Naturally there is considerable variety of tint among the many kinds of terre verte, but they all belong to the pale greyish class, and are more or less translucent, consequently their covering power is small. Their value lies in their durability, and the resistance they offer to the injurious effects of strong light and impure atmosphere. They can be employed either as oil or water colours. The only preparation to which the natural pigments are submitted is fine grinding and washing.

**TITANIUM GREEN.**—An excellent dark green pigment, though rather costly, can be prepared from rutile or any titaniferous iron ore by the following method :—

The ore is dressed clean, and fused with twelve times its weight of acid sulphate of potash in a crucible. When cool, it is reduced to fine powder, and digested at 120° F. in dilute hydrochloric acid (half water) until solution is complete. The hot solution is filtered off from the residue and carefully evaporated down to a syrupy consistence, when the nearly pure titanic acid is allowed to cool in the dish and thrown on a filter. When sufficiently drained, it is boiled in a large volume of water containing a little ammonia, and the precipitated titanic acid is filtered and washed.

If an ore is used containing carbonate of lime, it must first be treated with dilute hydrochloric acid before the sulphate of potash is applied.

The titanic acid on the filter is next mixed with a concentrated solution of sal ammoniac, and again filtered. Then it is digested in dilute hydrochloric acid at 120° to 140° F. till the solution is complete. On adding ferrocyanide of potassium to the acid liquor, and bringing quickly to a boil, a precipitate of ferro-cyanide of titanium is thrown down. This is very carefully and slowly dried, at a temperature never exceeding 200° F.

**VERDIGRIS.**—The chemical examination of verdigris shows it to be a basic hydrated acetate of copper, containing variable proportions of the bibasic and tribasic acetates.

Commercially it is prepared in districts where acetic or pyroligneous acid can be had at small cost. Thin pieces of scrap copper are subjected to the action of fermenting grape skins in mass, or cider refuse, for a fortnight or three weeks ; or to the influence of pyroligneous acid for four or five days. By this means the copper surfaces are attacked by the acetic acid being generated or liberated, and become coated with acetate of copper. At intervals the pieces are removed, and surfaces are cleaned of the accumulated acetate or verdigris, and this is repeated till the metallic copper has thus been completely converted. The collected verdigris is washed, and carefully dried at a very low temperature.

Its composition is subject to many irregularities, and the colour varies from green to bluish green according to the proportion of sesquibasic acetate present. It is one of the least permanent pigments, especially in the presence of water, and is exceedingly poisonous. At one time it was largely used as a pigment, but is now gradually going, if indeed it has not already gone, out of use. It can be distinguished by its solubility in acids and ammonia, the latter giving a deep azure blue solution. On being heated, it turns black, owing to its parting with acetic acid and leaving the black oxide of copper behind. This should be entirely soluble in nitric acid, the solution giving the characteristic tests for copper. The solution should give no precipitate with chloride of barium or nitrate of silver, and the original pigment should be freely soluble in any acid and in ammonia without effervescence.

**VERDITER.**—Green verditer is another of the copper greens which has practically disappeared from the modern painter's list of pigments. It is a yellow tinted very fugitive colour, consisting of a basic carbonate of copper, and is manufactured by treating copper solutions with carbonate of soda, or of potash.

**VERONA EARTH.**—One kind of terre verte (see p. 134), is

known by this name because it is produced in the neighbourhood of Verona.

**VICTORIA GREEN.**—This is a fancy name for the Brunswick greens compounded from Prussian blue, and already described on p. 114.

**VIENNA GREEN.**—The aceto-arsenite of copper described under the heading of emerald green (see pp. 121–125), is sometimes called by this name.

**ZINC GREEN.**—The pigments described under cobalt green (see p. 119), as often pass by the name of zinc greens, and in fact they contain much more zinc than cobalt.

A handsome but not permanent green may be made by combining zinc with iron instead of cobalt, in the form of a double cyanide. The process is as follows:—Finely powdered Prussian blue is stirred into a concentrated solution of chloride of zinc, and put by to allow the decomposition to take place. After some time, the precipitated ferro-zinc cyanide is thoroughly washed, and dried out of reach of the light.

## CHAPTER VI.

## REDS.

THOUGH the red pigments are an important class, they are not numerous, and, with the exception of a few lakes, they are drawn from the mineral kingdom. The most useful are compounds of the several metals, iron, lead, and mercury.

ANTIMONY VERMILION.—This useful pigment is prepared by several methods, as follows :—

(1) One of the earliest successful processes was that introduced by Mathieu Plessy, which gives a scarlet product. He obtains the pigment, a modified sulphide of antimony, by decomposition of hyposulphite of soda in the presence of chloride of antimony. The two solutions of hyposulphite of soda and chloride of antimony, each at 25° B., being prepared, the next step is to pour into a stoneware vessel 4 gals. of the antimony chloride solution, 6 gals. of water, and 10 gals. of soda hyposulphite solutions. The precipitate caused by the water is rapidly dissolved in the cold by the hyposulphite. The stoneware vessel is then placed in a hot water bath, and the temperature of the contents is thus gradually raised. At about 86° F. the precipitation of the sulphide commences, showing orange yellow at first, but becoming darker subsequently. When the temperature has reached 130° F., the vessel is removed from the water bath, and the deposition of the precipitate proceeds rapidly. The supernatant liquor is siphoned off, and the solid residue is washed first with water acidulated by adding to it one fifteenth of its bulk of hydrochloric acid, and then with clean water. Finally the residue is collected on a filter, and dried.

It is exceedingly brilliant while wet, but loses a portion of its brightness when dried.

Provision must be made for disposing of the sulphurous oxide gas driven off during the process of manufacture.

(2) Kopp found certain disadvantages in working by the above method, and adopted instead the reaction of antimony chloride upon a dilute solution of hyposulphite of lime.

Experiencing much difficulty in the decomposition of antimony sulphide by hydrochloric acid on an industrial scale, he experimented on roasting the sulphide at a moderate temperature in contact with air and steam, whereby most of the antimony sulphide is converted into oxide, while the sulphurous acid driven off is utilised for making the hyposulphite of lime. This proved a most successful plan, and the resulting antimony oxide is readily dissolved by commercial hydrochloric acid.

During the oxidation of the antimony sulphide, a certain proportion of antimonious acid may be produced. This is but slightly soluble in hydrochloric acid. It may be collected, however, by saving the residues from the treatment by hydrochloric acid, and washing them with chloride or hyposulphite of lime, which will dissolve the adherent antimony chloride; they are then dried, and melted with a little antimony sulphide and quicklime, so as to transform the whole into antimony green, the quicklime having the effect of decomposing any small residue of antimony chloride.

The preparation of the hyposulphite of lime is cheaply effected by the action of sulphurous acid on sulphides of lime, the sulphurous acid being derived either from the roasting of the antimony sulphide, or from pyrites or brimstone in the usual way.

Calcium polysulphide is prepared by boiling finely powdered sulphur and newly slaked lime in water. Certain advantages arise from the addition to this solution of a little powdered calcium oxysulphide, or some quicklime.

In the reaction of sulphurous acid on calcium sulphide and oxysulphide, sulphur is set free and forms a sulphite of lime, which, in the presence of sulphur and undecomposed sulphide, is soon transformed into hyposulphite, the reaction being facilitated by the rise of temperature which takes place in the apparatus.

As soon as the liquor has become slightly acid, it is drawn off into a large settling tank. If, after agitating for some time, the liquor has not become neutralised by the undecomposed calcium oxysulphide contained in it, this is brought about by addition of a little calcium sulphide, and is recognisable by the appearance of a black precipitate of sulphide of iron. After due settlement, the clear liquor is decanted, and forms a solution of nearly pure hyposulphite of lime.

The production of antimony vermillion is effected from the foregoing solutions of antimony chloride and hyposulphite of lime, in apparatus consisting simply of a series of wooden tanks raised conveniently above the floor, holding about 500 gals. each, and provided with steam coils for heating their contents.

Sufficient hyposulphite of lime solution is run into the tanks to fill about seven-eighths of their depth ; and then into the first tank is poured the chloride of antimony solution, in quantities of a few pints at a time. A white precipitate is formed, and rapidly dissolves at first ; when it is slow in going into solution, even though stirred, the addition of antimony chloride should be stopped, as an excess of hyposulphite of lime is essential. The liquor in the tank must be perfectly clear and limpid, and should any white precipitate remain it must be dissolved by making small additions of hyposulphite.

At this stage steam is admitted into the coils, and thereby the temperature of the solutions is gradually raised to 120° or 140° F., or even to 160° F., while stirring is unceasingly carried on. The reaction is soon manifested by the successive colours of the liquor, passing from straw-yellow to lemon-

yellow, orange-yellow, orange, orange-red, and lastly a very deep and brilliant red. The steam is shut off from the coil before the desired tint is arrived at, as the acquired heat and the agitation complete the development of the colour. If the heating is carried too far, the red gradually passes to a brown and later to nearly black. With experience, almost any desired shade of red can be produced.

When the precipitate has attained the required colour, it is allowed to settle, and the tank is covered. The clear and limpid liquor, having a strong sulphurous odour, is let out through tap holes at various levels in the sides of the tanks, and run by wooden gutters or leaden pipes into a large reservoir holding a quantity of sulphide and oxy-sulphide of lime. Here the sulphurous liquor regenerates a certain amount of hyposulphite of lime.

The antimony chloride solution always contains a large proportion of chloride of iron, which provides an easy means of guiding the progress of this latter operation. All the iron remains soluble in the mother liquors of the antimony sulphide, and as soon as they are brought into contact with the calcium sulphide, an insoluble black precipitate of iron sulphide is formed. So long as this remains, the mother liquors charged with sulphurous acid have not been added in excess; but when it disappears by conversion into soluble hyposulphite of iron, that is a sign that the sulphurous solution is in excess. The contents of the reservoir are then well stirred, and calcium sulphide is introduced if necessary, until the precipitate of iron sulphide returns and remains. It is also needful to ensure that a certain proportion of hyposulphite of iron shall remain in solution. The clear liquor decanted off when all the precipitate has gone down is a neutral solution of hyposulphite of lime, containing some calcium chloride and hyposulphite of iron.

Another requisite precaution in this regeneration of hyposulphite of lime is that no excess of calcium sulphide be left, or it will give an orange-yellow tint to the vermillion; and if

the hyposulphite of lime solution is alkaline and yellow, sulphurous acid liquor must be run in till all alkalinity is destroyed.

This regenerated solution of hyposulphite of lime is used like the first. The mother liquors charged with sulphurous acid are again neutralised in the large reservoir by new proportions of calcium sulphide and oxysulphide, until so much calcium chloride is present that they are useless for the purpose, say after 25 to 30 operations.

The antimony vermillion precipitated on the bottom of the first tank is received into a conical cloth filter, and the liquor drained off is passed to the reservoir. The first tank is then washed out with warm water, which also passes through the filter. The precipitate of red sulphide cannot be too carefully or completely washed, and finally is filtered and slowly dried below 140° F.

(3) Wagner's method of making a scarlet pigment is to dissolve 6 lb. of tartaric acid and 8 lb. of tartar emetic in 4½ gallons of water at 140° F., adding a solution of hyposulphite of soda at 40° Tw., and heating the whole mixture to 180° F., whereby the red pigment is gradually precipitated. It is collected on a filter, well washed and dried.

(4) The process adopted by Murdoch, in which a solution of antimony chloride (prepared by dissolving black sulphide of antimony in hydrochloric acid) is acted on by a current of sulphuretted hydrogen gas, has disadvantages in the apparatus necessary, in the limited range of tints which can be produced, and in the almost certain presence of free sulphur in the finished pigment.

Antimony vermillion forms an exceedingly useful pigment, which can be prepared in every shade of red, from orange to red-brown. It is produced in the condition of a very fine powder, requiring no grinding, and mixes readily with water or oil, especially the latter, and moreover does not interfere with the drying of the oil. It possesses great covering powers, and can be made at a low price. It undergoes no

change in strong light and impure air, and is insoluble in water, alcohol, essential oils, weak acids, ammonia, and alkaline carbonates ; but it is destroyed by high temperatures, strong acids, and caustic alkalies. It cannot be mixed with other pigments which are intolerant of sulphur, nor with alkaline vehicles. When pure, it should consist of nothing but antimony sulphide and a little water ; the presence of iron or lead indicates adulteration.

**BARYTA RED.**—An orange red may be prepared, according to Wagner, in the form of a sulpho-antimonite of barium, by calcining in a clay or graphite crucible at red heat for several hours a mixture of 2 parts of finely powdered barytes, 1 part of native antimony sulphide, and 1 part of powdered charcoal. The calcined mass is not removed until the crucible is quite cold, as it is liable to undergo combustion. When cold, it is boiled in water and filtered. The residue, containing some undecomposed sulphate and sulphide of barium, is utilised in the next batch. The pale-yellow filtrate is treated with dilute sulphuric acid, by which sulphuretted hydrogen is driven off, and an orange precipitate is thrown down. This is collected, washed on a filter, and dried, constituting the pigment.

**CASSIUS PURPLE.**—This costly pigment is a stannate of protoxide of gold, much used in painting on porcelain and for miniatures. It is the precipitate which is thrown down when solutions of gold and tin chlorides are mixed under proper conditions, according to one of the following methods :—

(1) Buisson prepares three solutions : [a] a neutral solution of protochloride of tin by dissolving 1 part of tin in hydrochloric acid ; [b] a solution (bichloride) of 2 parts of granulated tin in an aqua regia containing 3 parts of nitric to 1 of hydrochloric acid, removing the excess of acid ; [c] a neutral solution of 7 parts of gold in an aqua regia composed of 1 part of nitric and 6 parts of hydrochloric acid. The gold chloride solution is largely diluted with water, and to it is added the solution *b* of bichloride, and finally the solution *a*

of protochloride is introduced, a drop at a time, until the desired colour is produced in the precipitate. This last is rapidly washed by decantation, and finally dried away from the light.

(2) Figuier prepares a gold bichloride solution by dissolving 20 grammes of gold in 100 grammes of an aqua regia containing 4 parts of hydrochloric to 1 of nitric acid. The solution is evaporated to dryness in a water bath, and the residue is dissolved in 750 grammes of water. Into this solution, when duly filtered, pure granulated tin is introduced, and the whole is left for some days, at the end of which time all the gold will be in the state of stannate of protoxide; it is collected on a filter, carefully washed, and gently dried. The residues contain some gold, and should be preserved for subsequent operations.

CHINESE RED.—One of the many names of the chromate of lead pigment, described under Derby red, see p. 145.

CHROME ORANGE.—A popular name for the group of yellow-red pigments consisting essentially of lead chromate, and described under Lead orange, on p. 147.

CHROME RED.—Another of the synonyms for Derby red, see p. 145.

COBALT PINK.—This costly and permanent artists' colour is a combination of oxide of cobalt with magnesia. It is prepared by treating carbonate of magnesia with a concentrated solution of nitrate of cobalt; the resulting paste is dried in a stove, calcined in a porcelain crucible, and finally ground to a fine powder.

COBALT RED.—A very deep-coloured and permanent red pigment used in oil painting is the arseniate of cobalt, which is found native in admixture with other substances in cobalt mines, or may be artificially produced.

The native mineral is treated with boiling nitric acid; the solution is filtered clear, and small portions of potash are added till all the iron has been thrown down as arseniate. After this is completed, the mass is allowed to

settle, and the clear liquor is poured off. On adding further small portions of potash, the cobalt is also precipitated as arseniate.

To prepare artificial cobalt arseniate, grey cobalt ore (sulph-arsenide of cobalt), reduced to a powder, is mixed with a little sand and twice its weight of potash, and fused in a crucible. The slag of mixed sulphides which is formed is removed, and the remaining white arseniate of cobalt is pulverised and subjected to another fusion with potash. The slag is again removed, and the button of pure arsenide of cobalt remaining is finely powdered and again roasted to effect conversion into arseniate of cobalt. Lastly, it is ground very fine.

**COLCOTHAR.**—A fancy name for a kind of iron oxide pigment, described under oxide reds (see p. 150).

**DERBY RED.**—As a basic chromate of lead, often known as chrome red, Derby red is closely allied to chrome yellow, the preparation of which is described in a subsequent chapter.

It has been asserted that all the chrome reds, from the darkest cinnabar red to a lustreless minium red, are distinguishable simply by the size of the crystals composing the powder, as may be easily determined under the microscope, and that if various chrome reds of the same hue, but with different intensities of colour, are reduced by grinding to the same degree of comminution, the several powders will possess exactly the same degrees of intensity of coloration, though they lose in brightness. Therefore the conditions which give brilliancy and intensity of colour are those which favour crystallisation.

On this supposition it is recommended by Riffault to adopt a plan which dispenses with agitation, and he supports the following method :—

(1) Chrome yellow is precipitated in the usual manner, as described in a later chapter, without sulphuric acid, and is carefully washed. After draining, the mass is well stirred, and six or eight equal samples are drawn from it and put

into glass vessels of equal size and thickness of structure. To each sample is added a different volume of caustic soda or potash lye, marking about 20° B. For instance, to 5 volumes of paste are added 2,  $2\frac{1}{2}$ , 3,  $3\frac{1}{2}$ , 4, 5, &c., volumes of lye. The different mixtures are rapidly and thoroughly agitated, but the chemical reaction is allowed to take place without any disturbance. After examination of the quality of the products, the relative proportions of pulp and lye are noted down for the best hues obtained. Too much lye will fail to deepen the red colour; in fact, Derby red is entirely soluble in an excess of lye, and forms needle-like crystals holding potash when the caustic solution has absorbed carbonic acid from the air.

On the industrial scale the operation is conducted in a large tub, which receives the mixture of pulp and caustic lye in precisely the proportions found by experiment to give the best results. The changes in colour soon manifest themselves, and the whole reaction is completed in about 12 hours. At the end of that time, the lye is drawn off, and carries with it much of the chromic acid. The precipitated pigment is carefully washed with pure water once in the tub, and the mass is gently stirred. The washing is continued in the filters by throwing water upon the pulp, and in this manner there is less friction between the crystals, which retain their deep colour. Of course a highly crystalline dark red cannot possess great covering power.

(2) Prinvalt mixes together 100 lb. of lead carbonate and  $30\frac{1}{2}$  lb. of potash bichromate neutralised with caustic potash, in 50 gallons of water, leaving them in contact for a couple of days under repeated agitation. About half an hour's boiling then suffices to develop the red colour. After settling, the supernatant liquor is drawn off, and the precipitated pigment is washed twice with pure water and finally with acidulated water (1 lb. sulphuric acid in 10 gallons of water), and dried.

There are several other recipes published which differ in

detail from (2), but they do not demand a lengthy description.

(3) 100 lb. of lead carbonate (white lead) made into a paste with water, then added to and boiled with a solution of 50 lb. of potash bichromate and 15 lb. of caustic soda of 77 per cent. Remainder of process as before.

(4) 4 cwt. of lead monoxide (litharge) and 60 lb. of salt dissolved in 50 gallons of water, and left with agitation for 4 or 5 days; then boiled for 2 hours with solution of 150 lb. of potash bichromate.

(5) 100 lb. of lead carbonate (white lead) made into a paste with water, then added to a solution of 30 lb. of potash bichromate and  $12\frac{1}{2}$  lb. of caustic soda at 77 per cent., and boiled.

Derby red possesses great covering power and considerable brilliancy; but if not very carefully washed it is liable to retain a little alkali, which renders it unstable. Otherwise, it well resists damp, strong light, and impure air so long as sulphuretted hydrogen is absent. Taken altogether it is not one of the best red pigments, and its consumption is declining.

INDIAN RED.—This is one of the names for the red pigments due to oxide of iron, and is described under oxide red, p. 150.

LEAD ORANGE.—Equally well known as chrome orange, this pigment may be regarded as a Derby red in which the reactions have been curtailed. That is to say, the yellow normal lead chromate being in excess, the red chromate formed by the action of the alkali combines with that excess of the yellow salt and forms a yellow-red, i.e. orange. Obviously, therefore, a great variety of tints can be produced by altering the proportions of the alkali, and this is further regulated by the duration of the boiling, while the tint can also be weakened by admixture of barytes or gypsum. The better kinds of lead orange are prepared with the aid of caustic potash or soda as the alkali, while the cheaper sorts depend on lime. The operations are practically identical

with those adopted in the case of Derby red (see p. 145), the chief differences lying in the proportions of the ingredients. Thus :—

(1) *Pale*.—Add a thin cream made from 10 lb. of quicklime to a chrome yellow made from 100 lb. of lead acetate, 30 lb. of soda or potash bichromate, and 21 lb. of soda sulphate. Boil.

(2) *Pale*.—Add a thin cream of 10 lb. of quicklime to a chrome yellow made from 200 lb. of baryta sulphate, 100 lb. of lead acetate, and 35 lb. of potash bichromate. Boil.

(3) *Deep*.—Precipitate a chrome yellow by adding 35 lb. of soda or potash bichromate to 100 lb. of lead acetate ; settle. Draw off supernatant liquor and admit solution of 9 lb. of caustic soda at 77 per cent.

(4) *Deep*.—Add a cream of 10 lb. of quicklime to a chrome yellow made from 100 lb. of lead acetate, 75 lb. of baryta sulphate, and 35 lb. of potash bichromate. Boil,

In characters the lead oranges resemble Derby red (see p. 145.)

**MINIUM**.—The important red pigment known as minium or red lead is composed of two oxides of lead in combination, viz. about 65 per cent. of protoxide and 35 per cent. of binoxide. In its preparation, metallic lead is first converted by roasting into protoxide (termed “massicot,” “dross,” or “casing”) and this protoxide is further subjected to heat in a reverberatory furnace whereby a portion of it is changed into binoxide. It is also possible to produce red lead by the decomposition of the carbonate of lead (white lead) at a high temperature, but this does not seem to be an industrial process. The following methods are recognised :—

(1) The practice in France, as carried on near Tours, at the white lead works using the Thénard process, is to calcine the best metallic lead in reverberatory furnaces built in the rock. These furnaces are five in number, with double fire-places, four being constantly in operation, dealing with about 4000 lb. at a charge, and using bituminous coal as fuel. Each furnace is nearly circular in shape and about 11 feet in diameter, with a fire-place on each side of the hearth. The latter is constructed of fire-brick containing as little silica as

possible, and is made hollow so as to retain the metallic lead when the heat has rendered it fluid.

The products of combustion from the side fire-places, having heated the hearth and its contents, pass through an aperture in front of the charging door of the hearth, and thence go to furnish heat to an upper hearth where the conversion of the oxide into red lead takes place.

A period of about 12 hours is occupied in the oxidation of a charge, which is repeatedly "rabbled." Even then a considerable amount of the metallic lead remains unoxidised and is returned to the calciner with the next charge. Half the oxide is utilised for making white lead, as described in a later chapter, and the other half is converted into red lead by the method detailed hereunder.

The crude oxide is pulverised in a small mill and separated from the unconverted metal. The mill takes the form of a flat circular cast-iron plate on which rotates a cast-iron muller. Water and an agitating arrangement are also provided.

As the muller revolves the material undergoes comminution, and the small particles of oxide as formed are disturbed by the agitator and kept in suspension in the water, by the overflow of which they are continuously carried away into settling pits. The residual metallic lead is not pulverised, and of course never becomes suspended in the water, consequently it accumulates at the bottom of the mill, whence it is occasionally withdrawn for re-calcination.

Sufficient oxide having collected in the settling pits, it is transferred to a shallow pan heated by the waste heat from the furnaces and is there rendered almost dry. In this state it is put into small square dishes made of sheet iron, and adapted to hold about 30 lb. each.

A charge consists of a hundred of these dishes, which are placed in the heated furnaces at the end of each day. The roasting is repeated several times, and the product is accordingly known as "two fires," "three fires," &c.

The material at this stage is lumpy and coarse, and has to undergo dry pulverisation, the fine particles as they are produced being drawn off by means of a pneumatic fan, and collected.

(2) What may in contradistinction be called the English method of making minium does not differ materially from the preceding. The "drossing" furnace, where the metallic lead is first oxidised, receives a smaller charge as a rule, and perhaps greater care is given to the rabbling, and to the regulation of the temperature so that it is only just above the melting point of the metallic lead, and not sufficient to fuse the massicot.

Minium or red lead is one of the most important and useful red pigments, as it mixes well with oil, has good covering power, dries quickly, and is permanent except in presence of sulphur or sulphides.

ORANGE MINERAL.—The pigment known as orange mineral or orange lead is simply minium which has been imperfectly calcined. Consequently it is almost identical with red lead in composition, qualities, and method of manufacture, the only exception being that, as the calcination is not carried quite so far, therefore the colour is not so fully developed, and is an orange rather than a red. As with minium, practically the only adulterant is iron oxide red, which may be detected by boiling the pigment to a colourless solution with nitric acid, when addition of prussiate of potash will give a blue precipitate.

OXIDE REDS.—Under various names—such as Persian red, light red, Indian red, scarlet red, rouge, colcothar, red oxide, purple oxide, &c.—many pigments, of which the base is the ferric oxide  $\text{Fe}_2\text{O}_3$ , are now made. These vary in shade from a deep scarlet red to a dark violet. They are obtained both from natural and artificial sources. Oxide of iron occurs naturally as the mineral hematite, and some varieties of this are bright enough and soft enough to be used as pigment when ground up. These are usually nearly pure oxide of

iron. Then the ochres, when calcined, yield red pigments known as light red, Indian red, &c., and a good many reds are obtained from this source. The composition of these is variable, being dependent upon that of the ochres from which they are made, and these, as has already been pointed out, vary very much. Then, in preparing fuming sulphuric acid from copperas, oxide of iron which is specially sold as rouge, is obtained. Colcothar is produced as a residue; this is nearly pure oxide of iron, and usually has a red colour. In the manufacture of sulphuric acid from pyrites, a dark violet oxide of iron is left as a residue, and much of this is used as a pigment under the name of purple oxide. Then a large quantity of oxide of iron reds are made artificially from waste liquors obtained in copper refining, galvanising iron, &c. The composition of the oxide of iron reds, therefore, is very variable.

The whole group of oxide reds is of foremost importance, by reason of their good colour, covering power, and durability, besides which, being mostly bye-products of much more important manufactures, their cost is reasonable.

The methods of preparation of oxide reds vary slightly in detail according to the material from which they are made, but the general features of the processes are almost identical and eminently simple. The principal sources are impure native oxides of iron, such as the ochres, various waste liquors containing iron salts in solution, and copperas (protosulphate of iron).

(1) Native oxides. The iron present in the ochres and similar native earths exists in the form of hydrated oxide, and has a brown red colour. For many purposes this hue is satisfactory, and the preparation of such a pigment consists simply in grinding the mineral in a wet mill, subjecting it to levigation till all grit is removed, and drying.

In order to obtain a brighter red from the native oxides they must be calcined to effect dehydration. This can be

accomplished in the most rudimentary forms of furnace, and many kinds are in use. The colour produced depends on the degree and duration of the heat to which the material is exposed, the shade becoming deeper as the roasting is prolonged or the temperature increased. As no two samples of ochre are just alike it is impossible to fix a precise time for the length of the operation, and therefore it is necessary to repeatedly draw samples in order to judge of the progress of the dehydration and development of the colour desired. When the requisite shade is attained, the charge is drawn and allowed to cool.

(2) Waste Products. The pyrites cinders from sulphuric acid works afford an abundance of oxide of iron. When the pyrites has contained no copper, the cinders merely require grinding and levigating, the iron being present as oxide. But when the pyrites has been treated for the recovery of the copper, by a second roasting with salt, the liquors contain the iron as chloride and sulphate, and lime has to be added to precipitate the oxide. This last is dried and calcined in the same manner as the native oxides, and grinding and levigation can be dispensed with.

The liquors from galvanising works contain acid sulphate of iron (green copperas) in solution. To correct the acidity, more iron is added in the form of scrap. Then lime or other alkaline substance is introduced to throw down the iron as oxide, and this last is filtered out, dried, and calcined in the usual way.

(3) Copperas. Where beds of common iron pyrites occur, the iron sulphide is converted into sulphate by exposure to the oxidising influence of the air. The result is an acid sulphate of iron, which is leached out and neutralised by addition of more iron in the form of scrap. The neutral sulphate is crystallised out of the liquor, and calcined in a muffle furnace, the shade of the ultimate product being governed by the degree or duration of the roasting. The sulphurous acid liberated in the roasting is sometimes

utilised for making sulphuric acid, but is more often wasted, because, to be commercially successful, the sulphuric acid manufacture must be conducted on a large scale, demanding 100*l.* of capital for every 1*l.* necessary for the copper and red oxide fabrication.

PERSIAN RED.—A name which is used somewhat indiscriminately both for Derby red (p. 145) and for oxide red (p. 150).

REALGAR.—The native mineral realgar is a yellow-red bisulphide of arsenic, often called also ruby of arsenic, or arsenic orange. It occurs native in very limited quantities in some of the older rocks, and then only requires to be ground and levigated. But for painters' purposes it is prepared artificially by heating a mixture of sulphur and arsenic in such a way that they are melted in company and react on each other to form the arsenic sulphide. The heating takes place in crucibles, and the proportions are two parts by weight of arsenious acid (white arsenic) to one of flowers of sulphur. When the reaction has ceased, the contents of the crucible are allowed to cool, and then reduced to very fine powder.

The pigment is exceedingly poisonous and not remarkably durable, besides which, it cannot be mixed with any other pigment which is affected by sulphur.

RED LEAD.—A common name for minium, see p. 148.

ROUGE.—One of the names for a particular shade of the oxide reds, see p. 150.

VENETIAN RED.—A fancy name for a special shade of oxide red, see p. 150.

VERMILION.—This old pigment is gradually going out of use; the newer reds, which are more brilliant in colour and cheaper, are gradually displacing it, although it is doubtful whether it will ever go completely out of use. It is the mercuric sulphide  $HgS$ . When pure, it is not attacked by acids or alkalies; only aqua regia, a mixture of hydrochloric and nitric acids, is capable of dissolving it, when it forms a

clear solution. Heated in the flame of a Bunsen burner, it is completely volatile, a property possessed by no other pigment in common use, therefore any adulteration can be readily detected by simply heating a little vermillion in a crucible; if a known weight is taken and the residue is weighed, the amount of adulteration can be ascertained. Vermilion is chiefly adulterated with oxide of iron and orange lead. From the character of the residue left on heating in a crucible, the kind of adulteration can be readily ascertained.

(1) The following notes are taken from Christy's translation of a brochure on the Imperial Quicksilver Works at Idria, Krain :—

In the oldest times of the existence of the present works, vermillion was manufactured. In the beginning it was merely pure pulverised cinnabar ore, then later it was a product made by sublimation from this substance; and there were formerly other works for vermillion manufacture than those for quicksilver production. When the Venetians and Dutch began to produce better wares, the production here sank steadily.

The researches of Christofoletti, 1681, and of Baron Rich-tenfels, 1726, for the improvement of Idrian vermillion, met with as little success as those of some Venetian women—1740–1741—who had lost their husbands in the Venetian works and had offered themselves to manufacture vermillion according to the Venetian method.

After Hacquet had strongly urged the manufacture of vermillion, Oberhüttenmeister Ignaz v. Passetzky succeeded, with the Dutchman Gussig assisting him, in making beautiful cake cinnabar in 1782, and in 1785 vermillion also, in the newly-built works on the right bank of the Idriza.

In 1796 Oberhüttenverwalter (manager of the works) Leo-pold v. Passetzky introduced the sublimate and precipitate manufacture, but it was abandoned as unprofitable in 1824.

The many foreign attempts to manufacture vermillion in

the wet way caused similar ones here, as those of Fabriks-Controlor Rabitsch in 1838, and later of Hüttenverwalter M. Glowacki, which brought large amounts of the vermillion so manufactured into the market. Still this manufacture came to no full development, and became forgotten, until, finally, in the years 1877 and 1878, experiments led to its being discontinued on account of the costliness and uncertainty of the method. A new set of experiments in 1878 and 1879, by Assayer E. Teuber and Director of Works (Hüttenverwalter) H. Langer, under the direction of the Imperial Agricultural Ministry, led to favourable results. A new manufactory, set in operation in 1880, furnishes three sorts of vermillion manufactured in the wet way.

The arrangements of the works for the manufacture of vermillion in the dry way consist of:—One sulphur stamp battery. One amalgamating plant with eighteen small barrels; both pieces of apparatus being driven by a two horse-power water-wheel. Four sublimation furnaces, each with six retorts of cast iron. Four vermillion mills, each driven by a water-wheel of 2·5 horse-power. Kettles and vats for heating, digesting, and refining the ground cinnabar. One drying hearth. The preparation of vermillion as an article of commerce, falls into several separate operations, viz.:

1. Amalgamation; i. e. preparation of the raw mohr.
2. Sublimation; i. e. preparation of the cake cinnabar.
3. Grinding of the cake cinnabar, refining and drying of the vermillion.

For the preparation of the raw mohr, for each charge of eighteen kegs there are taken 80·64 kg. (117½ lb.) powdered and sifted sulphur, and 423·36 kg. (731½ lb.) of quicksilver.

The amalgamating kegs each contain 28 kg. (61½ lb.) of the charge, and are given intermittent rotating motion by a rack and pinion driven by a water-wheel. After an average of two and three-quarter hours, the amalgamation is complete, and the raw mohr is taken from the casks.

For the sublimation, four furnaces are used, each with six pear-shaped cast-iron retorts of considerable thickness. Each is charged with 58 kg. ( $127\frac{1}{2}$  lb.) of mohr, the mouth covered with a loosely placed sheet-iron helmet, the furnace being slowly fired; the combination of the sulphur and the quicksilver then results in about fifteen minutes, with a detonation. As soon as this operation (das Abdampfen) is over, a clay helmet is placed over the retort, and the firing is increased, so that after two hours and twenty minutes the excess of sulphur evaporates from the tube. The condenser is now added (Stückperiode—Cake-period) and luted, then the firing is still more urged, whereupon the cinnabar volatilises and deposits itself upon the glazed earthenware condensation apparatus (tube, helmet, &c.). After four hours, the sublimation is complete, and there is furnished by the helmet 69 per cent., by the tubes 26 per cent., by the condenser (Vorlage) 2 per cent., cinnabar.

The grinding of the cake cinnabar takes place in four mills driven by an undershot water-wheel. These mills have a fixed under and upper movable stone, and the grinding is done with water. The vermillion which leaves the spout and runs into glazed clay vessels has a temperature of about  $100^{\circ}$  F., that of the air being  $59^{\circ}$  F. The millstones make forty revolutions per minute, and after each passage of the charge are placed nearer together.

(2) A German chemist named Fleck has discovered that when a warm solution of hyposulphite of soda is added to a double salt of mercury, such as chloride of mercury and sodium, the solution becomes acid, and black sulphide of mercury is deposited. But if the hyposulphite solution is added in excess, and the temperature is not allowed to rise beyond  $140^{\circ}$  F., the solution remains neutral, and red sulphide of mercury, or vermillion, is deposited. The least quantity of acid causes the production of the black sulphide. The presence of a salt of zinc facilitates the production of the vermillion. The best method is as follows:—To four equiva-

lents of hyposulphite of soda mixed with four equivalents of sulphate of zinc in diluted solution, is added, drop by drop, a solution containing one equivalent of corrosive sublimate. The whole is gently heated for 60 hours, at a temperature of 112° to 130° F.

(3) The following account of vermillion manufacture in China appeared over the initials T. I. B., in the *Chemical News*.

The Chinaman has no knowledge whatever of chemistry, and of the principles of natural philosophy and statics generally his notions are of the most rudimentary and primitive description. How, then, in the face of these obvious disadvantages have the Chinese contrived to place themselves in the front rank amongst nations in the matter of certain chemical manufactures, one of the most important of which is the subject of this article—Vermilion?

We have seen with what ingenuity and pertinacity in carrying out his ends the Chinaman has succeeded in making perhaps the most delicate and perfect iron castings in the world. He has succeeded in that instance, not by any deep researches into the hidden mysteries of Nature, by no process of thought involving an enquiry into the “ reason why ” ; to this the Chinaman is averse, the whole tendency of his education, such as it is, tends to make him satisfied with observing effects ; it is sufficient to him to know that things are so, without going into troublesome or elaborate investigations into those changeless laws of Nature into which his philosophy teaches him that, as he cannot alter or control, research is fruitless : but that he has in his own small, ingenious, patient way observed effects to very good purpose, the unrivalled excellence of some of his manufactures testifies.

We will now enter a vermillion manufactory and watch the process from the first stage of mixing its two ingredients—mercury and sulphur—to the final process of weighing and packing this costly and beautiful pigment for the market.

The first objects to attract the visitor's attention on entering the yard attached to the works will probably be large piles or stacks of charcoal, crates or baskets of broken crockery ware, and numerous rusty old iron pans of somewhat similar shape to rice pans, but considerably thicker and heavier. There will also probably be a few broken and disused cast-iron mortars. All these articles are the cast off or worn out implements of the manufacture, and will be described in their proper order.

On entering the factory proper, scores of little stone mills, each being turned by one man, and other long rows of workmen weighing out and wrapping up the vermillion, will be seen. The furnaces are then arrived at: there may be a score or more in number, and may be ten or twelve in each furnace room, five or six on each side. After passing these, the stores of quicksilver, sulphur, alum, glue, new spare iron pans, serviceable crockery ware, and sieves and other utensils used in the factory are arrived at, and this completes the view of the works.

The iron pans in which the vermillion is sublimed are those referred to above; they are circular and hemispherical in shape; all are of the same size and weight; they are cast upside down, and in the casting, a runner or lump of iron, two and three-eighths inches in diameter by from six-eighths to one inch in depth, is purposely left on every pan in order to enable the workman the more readily to handle the pan when stirring up its contents. The size of the pans proved by actual measurement to be  $29\frac{1}{4}$  inches in diameter, by  $8\frac{7}{8}$  inches deep, and the weight 40 catties, or say about 53 lb.

These pans are set in rows of 5 or 6 on each side of a small rectangular room, in size some 12 feet by 15 feet; the door of this room is of wood and contains an aperture a few inches square in order to enable the workman to watch the progress of his operation, from time to time, without the necessity of lowering the temperature of the apartment by

opening the door. The pans are set in brickwork, each pan having beneath it a grate to hold the charcoal used as fuel. There is no communication between the grates or furnaces under each pan, and no chimney, the flames and products of combustion finding exit from the front of the grate, which is left wholly open at all stages of the operation.

The process of manufacture is as follows:—Taking an iron pan which is of 4 inches smaller diameter than those described, and also in all other respects proportionally less, except the runner, which is of the same size, a skilled workman proceeds to weigh out  $17\frac{1}{3}$  lb. of sulphur. This he places in the pan, and adds about half the contents of a bottle of quicksilver. The pan with its contents is then put upon a small earthen brazier or portable furnace, the fuel used in which is charcoal. When the sulphur is sufficiently melted, the workman, taking an iron spatula or stirrer, rapidly stirs up the quicksilver with the sulphur, and gradually adds the remaining contents of the bottle of quicksilver, stirring the two ingredients together meanwhile until the mercury has wholly disappeared, or “been killed,” as the Chinese put it.

When this takes place, the pan is removed from the fire, a small quantity of water is added, and rapidly stirred up with the contents of the pan, which have now assumed a dark blood-red appearance and semi-crystalline structure. This mass is then turned out of the pan into an iron mortar, and then broken up into a coarse powder. This forms a charge for one of the large pans previously described, and when sufficient material has been prepared to charge all the pans in one furnace chamber the sublimation is proceeded with as follows:—

All the pans having received their quantum of crude vermillion, this is covered with a number of crockery- or porcelain-ware plates, of tough, strong manufacture, each about 8 inches in diameter; some of these plates, however, are broken up, and are in a more or less fragmentary con-

dition. When these plates have been piled up into a dome-shaped heap of the same shape as the bottom of the upper pan, to which they should extend, the whole is covered with one of the smaller pans previously described.

Now it will be remembered that the smaller pan was of 4 inches less diameter than the larger one; there will consequently be a circular space two inches all round between the circumferences of the pans. Consequently the rim of the upper or covering pan will be about 2 inches lower than the rim of the lower pan; there will also be some 4 inches space horizontally between the rim of the large lower pan and that portion of the smaller pan which is at the same height as the rim of the larger one. This space is carefully filled with a clay luting into which some holes, generally about four in number, are pierced, extending down to the rim of the smaller pan or cover; this is done in order to allow the heated air and other matters to escape.

All the pans in one furnace chamber being thus charged and covered, the fires are lighted. The flames from the charcoal should occasionally play several feet above the mouths of the furnaces. The door of the chamber is kept closed, except when it is open for a moment in order to enable the workmen to replenish the fires, which must be kept up at a fierce heat for eighteen hours. During this process a blue lambent flame is seen to play above each of the four holes which are pierced through the clay luting of the pans, so it is evident that a considerable quantity of either one or probably both the ingredients is wasted. After eighteen hours the fires are allowed to go out, and the contents of the pan cool down.

When this is accomplished, the greater portion of the vermillion will be found adhering to the lower surface of the broken-up porcelain plates with which the crude product is covered. The vermillion is then carefully removed from the porcelain by means of chisels, and is now ready for the elutriating mills. Another portion of vermillion of not so

good quality is found adhering to the upper iron pan, and that obtained by washing the clay luting in a cradle, as diggers wash dirt for gold. This, together with the wipings and scrapings generally, is mixed up with alum and glue-water into cakes, and, after drying on a brick surface heated beneath by means of wood or charcoal, is powdered up on a mortar, and re-sublimed when a sufficient quantity has accumulated.

The vermillion which was removed from the porcelain plates is of a blood-red colour and crystalline structure. This is then powdered up in a mortar and removed to the levigating mills. These are the ordinary little horizontal stone mills used by Chinese and other natives of the East to grind rice and other grain into flour or pulp, as the case may be. Each stone is about  $2\frac{1}{2}$  feet in diameter; the lower stone is stationary, the upper is turned by a direct-acting piece of wood having a hole in it which works a wooden peg affixed to the upper stone, which is made to revolve by a backward and forward movement of the piece of wood, or handle, some 3 or 4 feet long, previously mentioned. One man turns each mill. The upper stone has a small hole in it near its centre, down which the workman from time to time pours a little spoonful of the powdered vermillion, which he washes down into the mill with water; as he turns the mill, the workman keeps continually ladling little spoonfuls of water down the aperture or hole in the upper stone; the ground and thus elutriated vermillion, as it escapes from between the stones, is washed down by the water into a vessel placed beneath to receive it.

When work is suspended for the evening, the ground vermillion is carefully stirred up with a solution of glue and alum in water, in the proportion of about an ounce of each to the gallon. The glue has been made to mix with the water by previously heating it with a small quantity of water; the earthen pots in which this process is effected each hold about 6 gallons. The mixture is then left to settle. In the

following morning the mixture of glue and alum is poured off the vermillion, and the upper portion of the cake of vermillion at the bottom of the vessel—that is, the portion which remained longest suspended in the liquid—will be found to be in a much finer state of subdivision than the lower portion, which requires to be again elutriated as on the previous day: this separation of the more finely divided vermillion from that which was coarser, by suspension in a dense medium, is a really most ingenious process, for which we should give the Chinaman every credit.

The process of grinding, elutriation, and separation of the coarsely ground from the fine vermillion, sometimes requires to be several times repeated, in order to fully bring out the colour. As a final process the damp cake of finely ground vermillion is stirred up with clean water, and allowed to settle down until the next morning, when the water is carefully poured off into large wooden vats to still further deposit a small quantity of vermillion yet remaining in suspension, and the vermillion is dried in the open air on the roof of the premises.

When quite dried, the cakes of now full-coloured pigment are carefully powdered, and sifted by means of square muslin-bottomed sieves, contained in a covered box some 2 feet high by  $2\frac{1}{2}$  wide, in which the sieves, which slide on a framework inside the box, are jerked backwards and forwards by means of a handle on the outside of the box or case containing them.

The now fully-prepared vermillion is removed to the packing house, where may be seen rows of workmen, men and boys, seated before a series of tables. Between every two workmen is a third, with a small pair of scales, which he holds in his left hand; and as the workmen on either side place before him the little pieces of paper in which the vermillion is to be wrapped up, he weighs into each paper one tael (about an ounce and a third avoirdupois) weight of vermillion; the papers are two in number, the

inner a black or prepared paper, and the outer a piece of ordinary white paper. After being wrapped up, the packets are placed in rows before another workman, who stamps them with a seal containing in Chinese characters the name and address of the manufactory in which the article has been made, and the quantity and quality of vermillion contained in the packet.

The rapidity and deftness of the Chinese workmen at this employment is really surprising; the stamping, for instance, is effected at the average rate of sixty impressions per minute, and the wrapping up is carried on with proportionate rapidity. The mixture of alum, which is the ordinary aluminium potassium sulphate, with the vermillion, in one of its stages of manufacture as described above, is not added, as at first sight we thought it might be, merely to assist in clarifying or purifying the water by causing it to deposit its sediment, but seems to have some peculiar effect upon the colour, although what may be the *rationale* of the process, or how it acts, we cannot quite clearly see. The glue is added as described above merely to favour separation of the finely elutriated vermillion by holding it longer in suspension than the coarser particles, which sink first, and may therefore be separated in their order of stratification.

The actual composition of vermillion is 100 parts of mercury to 16 of sulphur, when both these ingredients are in a perfectly pure state; the excess of  $5\frac{1}{3}$  lb. of sulphur added by the Chinese is probably volatilised and lost in the process of sublimation, or, as the sulphur used is generally not quite pure, a part may go for foreign matter contained in the sulphur; the balance being probably the *raison d'être* of the blue lambent flame seen playing over the apertures in the luting during the sublimation process. For a people having, like the Chinese, no acquaintance with even the first rudiments of chemistry, the proportion of ingredients taken— $56\frac{1}{4}$  catties to 13 catties, or say 75 lb. to  $17\frac{1}{3}$  lb.—shows wonderfully

accurate powers of observation and a knowledge of combining proportions only to be gained by much experience and a long extended series of careful observations highly creditable to the manufacturers. The entire process is one of the most ingenious and interesting to be seen in any part of the world.—(T. I. B.)

Another and briefer account of the Chinese vermillion manufacture is given by H. Maccallum, in the Proceedings of the Pharmaceutical Society.

He says there are three vermillion works in Hong Kong, the method of manufacture being exactly the same in each. The largest works consume about 6000 bottles of mercury annually, and it was in this one that the following operations were witnessed:—

First Step.—A large, very thin iron pan, containing a weighed quantity, about 14 lb., of sulphur, is placed over a slow fire, and two-thirds of a bottle of mercury added; as soon as the sulphur begins to melt, the mixture is vigorously stirred with an iron stirrer until it assumes a black pulverulent appearance with some melted sulphur floating on the surface; it is then removed from the fire and the remainder of the bottle of mercury is added, the whole being well stirred. A little water is now poured over the mass, which rapidly cools it; the pan is immediately emptied, when it is again ready for the next batch. The whole operation does not last more than ten minutes. The resulting black powder is not a definite sulphide, as uncombined mercury can be seen throughout the whole mass; besides, the quantity of sulphur used is much in excess of the amount required to form mercuric sulphide.

Second Step.—The black powder obtained in the first step is placed in a semi-hemispherical iron pan, built in with brick, and having a fireplace beneath, covered over with broken pieces of porcelain. These are built up in a loose porous manner, so as to fill another semi-hemispherical iron pan, which is then placed over the fixed one and securely

luted with clay, a large stone being placed on the top of it to assist in keeping it in its place. The fire is then lighted and kept up for sixteen hours. The whole is then allowed to cool. When the top pan is removed, the vermillion, together with the greater part of the broken porcelain, is attached to it in a coherent mass, which is easily separated into its component parts. The surfaces of the vermillion which were attached to the porcelain have a brownish red and polished appearance, the broken surfaces being somewhat brighter and crystalline.

Third Step.—The sublimed mass obtained in the second step is pounded in a mortar to a coarse powder, and then ground with water between two stones, somewhat after the manner of grinding corn. The resulting semi-fluid mass is transferred to large vats of water and allowed to settle, the supernatant water is removed, and the sediment is dried at a gentle heat; when dried, it is again powdered, passed through a sieve, and is then fit for the market.—*Proc. Pharm. Soc.*

(4) Firmenich describes a process which he declares gives better results in the beauty of colour than any other. It consists in using sulphide of potassium, which must be in a state of great purity. Of the various methods for preparing potassium sulphide, Firmenich rejects those in which caustic potash lye is boiled with excess of flowers of sulphur, on account of the simultaneous formation of a hyposulphite or sulphate of potash, which interferes in the preparation of the vermillion.

The process adopted by Firmenich for making pure potassium sulphide is to reduce sulphate of potash by heating with charcoal, and subsequently saturating the lye with sulphur to the necessary degree.

Usually about 20 parts by weight of potassium sulphate and 6 parts by weight of charcoal are reduced to very fine powder and thoroughly incorporated. Placed in a Hessian crucible, the mass is covered, luted, and strongly heated.

As considerable ebullition takes place the crucible should be of such a size that the charge only occupies two-thirds of its capacity. After fusion is complete, the mass, which is now potassium sulphide, is allowed to cool; it presents a reddish-brown crystalline appearance, and is very hygroscopic. It is put into a cast-iron pan, with addition of soft water in the proportion of 7 parts of water to every 2 parts of the potassium sulphide; after boiling, it is filtered, and on cooling, the undecomposed sulphate of potash collects in crystals attached to the sides of the pan.

The thus purified lye is boiled a second time with flowers of sulphur, added in small doses until saturation is indicated by bubbling and effervescence. The simple (monosulphide) potassium sulphide in this manner takes up four additional atoms of sulphur, and becomes the penta-sulphide.

The preparation of the vermillion then proceeds in the following manner:—Into a series of large flasks are put 11-lb. of mercury, 5 lb. of the potassium sulphide lye, and  $2\frac{1}{4}$  lb. of sulphur. The contents are subjected to a moderate heat, and the flasks are then agitated in a curious manner by arranging them in pairs in baskets suspended from strings, over a straw mattress, on which the baskets bump each time they descend.

Occasionally the flasks are turned about, and after about two hours of this agitation they commence to grow hot, and the contents assume a greenish-brown colour. The lye is robbed of its sulphur by the mercury, and replenishes itself from the excess added.

Complete combination of the mercury and sulphur is accomplished in about three and a half hours, when the colour of the mass becomes dark brown. The next step is to cool the compound, an operation which must proceed very slowly, and should occupy about five hours.

Development of the colour is effected by heat, for which purpose the flasks are placed in a stove room or water bath,

and subjected to a temperature which does not fluctuate beyond 113° and 122° F., under the influence of which the red colour appears. The greatest care is necessary in this heating process, as it determines the success or failure of the colour. It lasts several days, during which the flasks should be shaken three or four times daily.

In order to separate the vermillion from the excess of sulphur, water is added to the contents of each bottle, and, after thorough shaking, the whole is turned out into a filter. The clear liquor escapes, and the residual vermillion is mixed with caustic soda lye in stoneware jars, and thus the remaining free sulphur is dissolved out. Subsequently the lye is poured off as completely as possible, and the deposit is repeatedly washed, first by decantation and finally on a filter. The whole operation of filtering and washing cannot be completed in less than two or three days. When this is finished, the drying must be carried on at a very low temperature, till the vermillion can readily be broken and is dry to the touch, when it is put into iron basins and repeatedly stirred, while the temperature is allowed to reach 143° F., but never beyond that. The final desiccation occupies about five hours.

Vermilion made in this way is reputed more permanent and less costly than by the usual methods.

(5) Dutch vermillion has a good name, and one method adopted in Holland is as follows:—A mixture of 2 lb. of mercury and 1 lb. of sulphur is thoroughly ground, and to 100 lb. of the mixture are added  $2\frac{1}{2}$  lb. of minium or of granulated lead. About 2 cwt. of the compound is put into each sublimation pot, which is duly heated. When the operation is finished, the pots are allowed to cool for eighteen to twenty hours, when they are broken, and their contents are ground in a mill. The lead remains as a sulphide in the bottom of the pots.

(6) A modification of the Dutch method consists in making an intimate mixture of 54 lb. of mercury squeezed

through chamois leather and  $7\frac{1}{2}$  lb. of flowers of sulphur, which is then moderately heated on a shallow iron dish, and the resulting black sulphide ("ethiops") is coarsely broken, ground, and kept in pots. To convert the ethiops into vermillion, the former is put into large clay crucibles in a furnace, and heated to dark-redness, whereupon the mass takes fire. As soon as the flame has subsided, the crucibles are covered with a close-fitting iron plate, and the firing is continued for thirty-six hours. The mass is stirred every half-hour with an iron rod, and fresh additions of ethiops are made at four or five hours' intervals. The vermillion is sublimed, and condenses on the cool portion of the interior of the crucibles, whence it is collected by breaking the crucibles when cold, and is finally ground and levigated.

(7) Kirchoff's method requires special care, and consists in grinding 300 lb. of mercury with 68 lb. of flowers of sulphur in a mortar, the sulphur being first moistened with a few drops of caustic potash. The resulting black sulphide of mercury is added to 160 lb. of caustic potash dissolved in very little water, and the whole is heated for half an hour on a sand bath, with occasional addition of water to make up for loss by evaporation. Gradually the mass, under constant agitation, becomes brown and gelatinous, and finally red. Thereupon it is carried to the stove room and still agitated at intervals. After several washings it is drained, and dried very gently.

(8) Weshle mixes finely powdered cinnabar with 1 per cent. of antimony sulphide, and boils the mixture several times with three parts of potassium sulphide in a cast-iron pot. The precipitate is water-washed, digested with hydrochloric acid, washed again, and finally dried.

(9) Jacquelin takes 90 lb. of mercury, 30 of sulphur, 30 of water, and 20 of hydrated potash; the mercury and sulphur are put into a shallow cast-iron dish, dipping into cold water, and the potash solution is added by degrees while the mass is kept in agitation. Then the mixture is heated for an

hour at 176° F., the evaporated water being replenished. The vermillion is washed in an excess of boiling water, and again several times in cold water, and finally filtered and dried.

VICTORIA RED.—One of the fancy names for Derby red. (See p. 145.)

## CHAPTER VII.

## WHITES.

IN the whole range of pigments there is no more important class than those to be described in this chapter. Not only are the white pigments largely employed for the sake of their distinctive colour, but they are probably even more extensively applied as a basis of other pigments, both as an ingredient in the composition of the other coloured paints and for ground coats where the final coat is to be of a delicate shade. They are among the cheapest and most permanent pigments, and possess as a whole remarkably good covering powers.

BARYTA WHITE.—Barytes or sulphate of baryta, the most important of the salts of barium, is found native in large quantities, forming the species of mineral termed barites or barytes, and commonly known as heavy-spar, on account of its weight (sp. gr. from 4·3 to 4·7). It is found in Derbyshire and Shropshire, and often occurs in fine tabular crystals. The massive variety found in the mountain limestone of the above counties is sometimes called “cawk”; it is more frequently found in white or reddish-white masses. In Saxony it occurs as the mineral *stangen-spath*, in a columnar form; and at Bologna, a nodular variety is found, called Bologna stone, which is notable for its phosphorescent powers when heated.

The pure salt may be prepared artificially for use as a pigment, by adding dilute sulphuric acid to a solution of chloride of baryta, when a white precipitate is formed; this is well washed and dried. It is a heavy, white powder, insoluble in water and nearly insoluble in all other menstrua. It may also be prepared by heating the native

mineral, grinding it to powder, and well washing it, first in dilute sulphuric acid, in order to remove any traces of iron, and afterwards in water; the white powder is afterwards thoroughly dried. This process is employed at several works in the neighbourhood of Matlock Bath, in Derbyshire, but much larger quantities could be produced in different parts of the country if the demand for the article rendered its production more profitable. The principal use of sulphate of baryta is to adulterate white lead, and to form the pigment known as *blanc fixe*, or permanent white. For these purposes, the native mineral, ground and washed as described above, is commonly employed.

Improvements in machinery and in the process of treating natural barytes have overcome many of the objections which formerly existed to its utilisation, and considerable attention is now being given to the localities in the United States where it is found. The mineral, in order to be available for the uses to which it is put, must be fairly free from quartz grains, the stain of iron rust, and other impurities. If the barytes is stained to any extent, it is practically valueless, as a good white colour is essential to its usefulness. Quartz grains or other hard substances with which it is apt to be associated injure the machinery in grinding. The purest barytes so far produced in America comes from Missouri, though a very fair grade is now being mined in considerable quantities in Virginia.

The returns from all producers of crude varieties show a product in the United States, for 1889, of 21,640 short tons, valued at 106,313 dols., against 20,000 short tons in 1888, valued, approximately, at 110,000 dols. The product was limited to four States, as shown in the following table:—

	Short tons.	Value.
Illinois .. .. .. ..	200 ..	\$1,300
Missouri .. .. .. ..	7,558 ..	32,715
North Carolina .. .. .. ..	3,000 ..	15,000
Virginia .. .. .. ..	10,702 ..	57,298
Total.. .. .. ..	21,460	\$106,313

PLANC FINE.—This name is given to baryta white when it has been artificially prepared by adding sulphuric acid to a solution of chloride of barium. (See p. 170.)

CHARLTON WHITE.—One of the names applied to a white pigment, containing zinc oxide and sulphide, and described under zinc whites, p. 254.

CHINA CLAY.—This substance is also known as kaolin, porcelain clay, and Cornish clay. It arises from the natural decomposition of felspar in soft disintegrating granite, gneiss, and porphyry, the rocks which are rich in soda-felspar yielding it most abundantly. The main supplies of this country are derived from Cornwall and Devon ; in continental Europe, beds of good quality exist in France, Bavaria, Saxony, Prussia, Bohemia, Bornholm island, and Hungary ; in China, it is very plentiful ; and in the United States, it occurs in many localities.

The approximate composition of china clay may be stated as silica, 47·2 ; alumina, 39·1 ; water, 13·7 per cent. Often a little iron, lime, and potash or soda are left in the prepared article by the imperfection of the cleansing process. The most important characters are colour, plasticity, and a capacity for hardening under the influence of heat.

The china-clay industry of Cornwall and Devon has been admirably described by J. H. Collins, F.G.S., in a paper recently read before the Society of Arts.

*Occurrence.*—The natural clay rock is almost always covered with a thick layer of stones, sand, or impure and discoloured clay, known as “overburden.” This capping often much resembles glacial drift ; but it never contains any scratched or glaciated stones, or travelled blocks. It varies in thickness from 3 feet to 40 feet, and must, of course, be removed before the clay can be wrought. The clay rock, being a decomposed granite, consists of china-clay, irregular crystals of quartz, and flakes of mica, with sometimes a little schorl and undecomposed felspar.

*Extraction and Preparation.*—The following descriptions apply, with more or less accuracy, to a majority of the larger works of the present day, turning out from 2500 to 8000 tons of clay each, yearly. Two somewhat different methods are employed, according to the situation of the “bed” of clay in relation to the surface contour of the immediate neighbourhood. The most general case is that in which the clay has to be raised from a veritable pit, the bottom of which is lower than the ground on all sides. The exact situation of the clay is first determined by systematic “pitting,” to a depth of several fathoms, or occasionally by boring. A shaft is then sunk either in the clay itself, or, preferably, in the granite close to the clay. From the bottom of this shaft, a level is driven out under that part of the clay which it is intended to work first, and a “rise” is put up to the surface, which should, by this time, be partially cleared of its overburden. A common depth for such a shaft will be from ten to twelve fathoms. As soon as the rise is completed to surface, a “button-hole” launder is placed in it, and the remainder of the rise is again filled up with clay. In the meantime, a column of pumps has been placed in the shaft, with an engine to work them, unless water-power is obtainable.

For water, many works are almost entirely dependent upon that met with in sinking the shaft and in driving levels; but, of course, this may be, and is, eked out by catching the rain-water in reservoirs, and by making use of such small streams as may happen to be available. A small constant supply is sufficient even for a large work, as it is used over and over again. The operation is begun by digging a small pit in the clay, around the upper end of the button-hole launder, and running a stream of water over the exposed clay, or “stope,” which is broken up with picks. A very large quantity of sand is constantly disturbed, and as constantly shovelled out of the way, while the water, holding the clay and finer impurities in suspension, runs

down the launder, along the level, and into the bottom of the shaft, from whence it is pumped up by the engine or water-wheel.

As the excavation becomes larger and deeper, more overburden is removed, and the upper portions of the launder are taken away, until at last the stopes reach the level, when the launder is, of course, no longer required. At first, the sand is thrown out by one or two "throws," but very soon it becomes necessary to put in an inclined road, for pulling up the sand in waggons; these are worked by a horse-whim, or by winding gear attached to the engine or water-wheel. As there are from three to eight tons of sand to each ton of clay, its removal in the cheapest possible manner is a matter of great importance. Any veins or lodes of stone, or discoloured portions of clay, are raised from the "bottoms" in the same way as the sand. The stream of water, holding in suspension clay, fine sand, and mica, is, in well-arranged works, lifted at once high enough to allow of all subsequent operations being carried out by the aid of gravity.

The stream is first led into one or two long channels, the sides of which are built of rough stone. In these channels, called "drags," the current suffers a partial check, and the fine sand and rougher particles of mica are deposited. From these drags, the stream passes on into other channels, much resembling them, but of greater number, so as to divide the stream still further. This second series of channels, known as "micas," are often built of wood, but sometimes of stone. They differ in no essential respect from the drags, but are more carefully constructed and better looked after, and, as the stream is greatly divided and very gentle, the fine mica is deposited in them. The micas are often about 11 inches wide, ten or a dozen in number, and 100 feet or more long. Provision is made, by underground channels and plug holes, for the periodical cleansing of the drags and micas. This may have to be done twice a day, but generally only once.

The deposit in the drags is worthless at present, and is always thrown away; but that from the micas is often saved, and sold as inferior or "mica" clay. The refined stream of clay then passes on to the "pits," which are circular, 30 to 40 feet diameter and 7 to 10 feet deep. These pits are built of rough masonry, and have an outlet at the bottom, opposite the point at which the stream of clay-water is admitted. This outlet is stopped by a gate or "hatch," or by a plug, and is kept closed until the pit is full of clay. In each outlet, however, is fixed an upright launder some 4 inches square, provided with "pin-holes" and wooden pins set close together. As the stream of clay enters on one side, it is constantly depositing its burden, and the water is as constantly drawn off nearly or quite clear from the pin holes, the pins being put higher and higher as the clay rises in the pit. The effluent water is conducted directly to small storage reservoirs, and thence over the clay stopes, whence it does its work over again.

When the stream of clay-water enters the pits, it contains from  $1\frac{1}{2}$  to 3 per cent. of clay; and what is called a good washing stream will carry about one ton of clay an hour. When the pit is full, the "hatch" is drawn, and the clay is "landed" into the tank. The upper portion is sufficiently fluid to run in of itself; but that near the bottom has to be helped out by men using "shivers" of wood or iron, which resemble large hoes; they are assisted by a small stream of water. The tanks are commonly, but not always, rectangular, built of stone, and paved with stone at bottom, often 60 feet by 30 feet by 6 feet or larger. Once in the tank, the clay is left to settle, until it has the consistency of cream cheese, the water being drawn off from time to time; it is then ready to be trammed into the "dry."

The "dry" is a large building erected in immediate proximity to the tanks. It is always composed of two parts, the dry proper and the "linhay." The floor or "pan" of the dry is composed of fire-clay tiles 18 inches square, 5 or 6 inches

thick at the fire end, and gradually thinning off to 2 or  $2\frac{1}{2}$  inches at the stack end. The flues are built of fire-brick, about 15 inches wide, 2 feet deep at the fire end, and 9 inches deep at the stack end. Each flue should be supplied with a damper. The furnaces are built in and arched over with best fire-brick ; the fire bars run longitudinally, and are about 6 feet long. The grate surface is about 2 feet 6 inches wide in front, and 4 feet 6 inches to 6 feet at back, according as each furnace supplies three or four flues.

The clay, brought in from the tanks in tram-waggons holding about half a ton, is tipped on to the tiles, and spread in a layer from 9 inches thick at the fire end to 6 inches thick at the stack end. The fire end is loaded and cleared every day ; the other end perhaps twice or thrice a week, according to the length of the dry, thickness of tiles, perfection of draught, &c. An average size for a first-class dry is perhaps 15 feet wide and 120 feet long ; but some have been constructed considerably larger than this. The pan of the dry should be 6 or 8 feet above the linhay whenever possible, so as to afford storage space for the dry clay, without expending labour in piling. The tiles should be as porous as possible, for very much more water passes through the tiles and into the flues than is driven upwards in the state of steam. The temperature should never be allowed to rise so high that the workmen cannot walk on the tiles, otherwise the clay may become baked and damaged.

In cases where there are no means of artificial drying, as at some old-fashioned works, the thick clay is at once transferred from the original settling pit to shallow depressions in the ground, called "pans." Ten or twelve of these, each holding from 40 to 50 tons, should be provided for each settling pit ; they measure from 20 to 40 feet square, and 2 feet deep, and are enclosed by granite walls, the interstices of which are rendered impervious by plugging with moss. The clay, filling two-thirds of their depth, is here left ex-

posed to the sun and wind, by which it is partially deprived of its moisture.

In order to complete its desiccation, the clay is removed from the pans after three or four months' exposure. A number of parallel incisions are made lengthwise in the clay, by means of a knife attached to a long handle; the strips are next divided transversely, by men with spades, who throw the blocks on to a board, upon which they are borne by women and children to the sandy drying yard, where, in fine summer weather, they soon become dry. They are then collected, and piled away in sheds, under a number of thatched gates or "reeders," or are placed in some sheltered position where air can circulate around them without their becoming wet from rain.

When required, the blocks are scraped by women armed with hoes, before being despatched from the works. The transport is often effected in small casks, holding about half a ton. A few years since, a machine for drying china-clay was invented by a mechanical engineer named Leopoldo Henrion, of Sampierdacena, near Genoa. It is said that, by its use, the operation can be effected in a few hours, at a relatively small cost.

Collins was first led to adopt his arrangement in consequence of the formation of the ground; but he is inclined to recommend it in most cases if practicable. Very large quantities of stone are required in the dry pits, tanks, &c. Very often this is got, in part or entirely, in the process of excavating the pits, &c.; but if it cannot be so obtained, a very serious expense will be incurred, in some instances amounting to several thousand pounds. The total cost of the works may even be doubled from this cause, if stone has to be fetched from a distance of several miles.

Two modes of building with rough stone are adopted; they are known as "lime building," and "dry stone walling." The first needs no special remark, but the second is very ingenious and very effectual. The wall is built up double,

with a batter of about  $\frac{3}{4}$  inch or 1 inch to the foot. Moss is placed between the joints of the wall, and the space between is filled in with sharp sand, the refuse of that or some other clay works. A small stream of water is then made to flow over the sand, which is well beaten in with rammers, or by treading with the feet. This process is continued, a foot at a time, till the wall reaches the required height, when it is either paved with rough stones set on edge, or turfed. A wall properly built, in the manner just described, is quite impervious to moisture, and will stand for fifty years or more. It is, where the proper kind of sand is abundant, much cheaper than lime walling, and is always preferred for the walls of pits and tanks.

Where the bed of clay is situated on a hill-side, with plenty of space below, a tunnel is driven in from the hill-side or from the valley to the required depth, and a rise is put up as before. This rise is then divided off into two parts. In the smaller, a button-hole launder is placed as before, and packed around with clay; but the larger is left open. A stream of water, obtained by pumping or otherwise, is made to run over the stope, and down the button-hole launder. It then flows along a launder placed in the bottom of the level, until it makes its exit in the valley. It may then be purified, settled, and dried exactly as already described--the works being laid out at a lower level than the adit; or, if the clear water is wanted to flow over the stope, or it is, for any reason, necessary to place the pits and tanks at a higher level than the stopes, the water is pumped up after partial or complete purification.

The main difference in this mode of working is that instead of pulling the sand and rubbish up over an incline, it may be tipped down the pass into waggons, run out through the level, and tipped over the hill-sides. In cases where waste water is abundant, it may even be washed out at night, thus saving the expense of tramping. Of course, when the workings have reached their full depth, the rise and the launder

are dispensed with, and the adit level communicates directly with the "bottoms." By this mode of working a considerable economy may be effected, especially when it is not necessary to pump the clay water for settling or repeating.

*Cost of Production.*—Where the conditions of production vary so greatly, there must necessarily be great differences of cost; but, after having been at some pains to determine the cost under average conditions, Collins thinks the following figures and statements may be relied upon. A work capable of producing say 4000 tons of clay yearly will cost from 2500*l.* to 5000*l.* To get the clay in the linhay ready for the market will cost about 9*s.* a ton, of which about 2*s.* 6*d.* must be expended in fuel for pumping and drying, 1*s.* in removing overburden, 1*s.* in removing sand, and 1*s.* for management and office expenses, leaving 3*s.* 6*d.* as the net labour cost of washing and drying a ton of clay. To the 9*s.* net cost of clay must be added an average of 3*s.* for royalties, 4*s.* for transit and placing on board ship, and 1*s.* for agencies, commission, bad debts, and sundries, making the average actual cost amount to 17*s.* Some favourably situated works can no doubt save 2*s.* or even 3*s.* on this account; in others, the cost may amount to 20*s.* or even 22*s.* As to the selling price, this varies much more widely than the cost of production, ranging from 14*s.* to 35*s.* *f.o.b.* Clays sold at the lower rate are unremunerative.

*Nature and Utilisation of Waste Products.*—Besides the clay proper, there are certain waste or pseudo-waste substances produced in very large quantities. These are as follows:—

Fine Mica.—This is deposited in the "micas"; a few years since it was thrown away, or rather washed away, as is still the case in many works. Sometimes, however, it is collected, dried in the manner of clay proper, and sold to the makers of soft paper, paste-board, inferior pottery, &c., at a low price.

Coarse Mica.—This is invariably washed away, or thrown

away, there being at present no demand for it. It, however, contains a very beautiful material, which might be applied to many ornamental purposes.

Sand.—This consists of broken quartz crystals, mostly white or pale brownish ; when washed clean, it is the finest building sand known, as the angles are all sharp. Mixed with one-eighth of Portland cement, it forms a concrete as hard as stone.

Discoloured Clay.—This has to be dug out from among the good white clay in many places. It has been successfully used in the manufacture of white bricks for building purposes. In some instances, a quantity of the sand already mentioned is mixed with the refuse clay, and produces an excellent fire-brick. The same material is used in the manufacture of the tiles used as a floor for drying the clay. The manufacture of bricks and tiles from this debris is a growth, it is believed, of the last twelve years.

Overburden.—The upper part of this consists of soil, or "meat earth" ; this is usually removed and carefully preserved. Underneath is a hard, often stony or sandy layer, which, in districts where tin is worked, often contains enough tin to pay for washing. With this stony or sandy layer, is usually a considerable thickness of discoloured clay suitable for brick-making.

Branches.—These are stony veins which run through the clay stopes in various directions. Sometimes they are quite worthless ; but in a few instances they are veritable tin lodes, and contain enough tin to pay for stamping and dressing. Thus at Carclaze, near St. Austell, each 1000 tons of clay yields something like one ton of oxide of tin, and formerly the proportion was much greater. The proportions of these waste materials, as compared with the fine clay procured, are thus stated :—

For every 1 ton of fine clay there is removed—from 3 to 7 tons of sand, average about  $3\frac{1}{2}$  tons ; from 2 to 5 cwt. of coarse mica, average 3 cwt. ; from 1 to 3 cwt. of fine mica,

average 2 cwt.; from 0 to 1 cwt. of stones, average  $\frac{1}{4}$  cwt.

A cubic fathom of clay rock, of average quality, will yield about  $2\frac{1}{2}$  tons of fine clay; and about half a fathom of overburden must be removed to get it.

*Suggested Improvements in Preparing.*—Collins thinks that there is still much room for improvement in the preparation of china clay, but that such must be a growth of time and circumstances. At the present time, about one ton of water has to be driven off from each ton of clay in the “dry,” and this uses at least 2 cwt. of coals on an average, and costs from 8d. to 10d. in labour. In a few modern drys, a small economy in fuel has been effected by lengthening the kiln; but in none has it been brought so low as  $1\frac{1}{2}$  cwt. to the ton of clay.

Stocker, in 1862, suggested the use of filter beds, and also devised a centrifugal dryer; but neither of these contrivances has come into use, and the first would seem quite inapplicable on account of the extreme fineness of the particles of clay, and the impermeability of even a thin layer of that substance. Some economy might perhaps result from the use of hydraulic filters of calico, such as are used in the potteries for drying the slip; but it is very doubtful if any saving would be effected, as the labour would be about the same, and, against the 2s. a ton for fuel, would have to be placed the wear and tear of the calico.

In washing the clay from the stope, some benefit might accrue from the use of a jet of water under a pressure of from 50 to 100 lb. per square inch, as in the so-called hydraulic mining. This could only be applied to stopes of even quality, where very little picking out of inferior portions was required; but it would supersede the services of the “breakers” on the stope, and greatly lessen the labour of the washers. It is but rarely that a natural head of water is obtainable equal to the required pressure; but where machinery is used for pumping, the additional cost of pumping, say 250 gals. a

minute to a height of 150 feet in a standpipe, would be very slight, as the extra power required is little more than that of one horse.

*Statistics.*—From statistics obtained from many sources, it is evident that the production has very largely increased from 1809 to 1874—2919 tons against 226,309. In 1810, Trethosa (one of the largest works) produced 300 tons per annum, and employed thirteen persons, viz. eight in removing burden and raising (breaking) clay (at per fathom), three washing, two attending ponds and packing. In 1874, one of the works near St. Austell produced 9000 tons, employing about thirty men. Many works produced 6000 tons, employing twenty men. The quantity sent annually from Cornwall must average at least 150,000 tons. It goes not only to Staffordshire, but also largely to France, Belgium, and other countries. The extensive clay works recently opened in several departments of Northern France have done much to curtail the export of Cornish clay to that country, and the large deposits of the island of Bornholm have lately been worked upon to supply the needs of Denmark, Sweden, and Germany; while similar utilisation of native clays has been carried out in America. Nevertheless, the growth of home industries which depend in a measure upon this article will, doubtless, counteract the influence of decreasing exports.

*Artificial China Clay.*—The principal supplies of china clay are obtained, as has been described, through the agency of natural decomposing influences in granite rocks. In one instance, however, at Betleek, County Fermanagh, it is procured by calcining the red orthoclase granite of the district. The felspar is whitened by the process, and the iron becomes separated in a metallic state, and is removed by magnets.

*Characters.*—Being virtually a hydrated silicate of alumina, china clay is a remarkably stable pigment. Not only is it unaffected by prolonged exposure to strong light and impure air, but is insoluble in water, weak acids, and alkalies. It

is moreover very much lighter in weight than any other white pigment, an advantage on the score of cost when buying by weight. Its covering power in distemper work and as a water colour is good; but the addition of oil reduces its capacity. The best qualities are exceedingly fine in grain and pure in tint, but inferior samples sometimes have their yellowness "corrected" by the addition of a little ultramarine.

**ENAMELLED WHITE.**—Another name for the finest kinds of baryta white, see p. 170.

**ENGLISH WHITE.**—A synonym for whiting, see p. 246.

**GYPSUM.**—This very common and abundant mineral is a hydrated sulphate of lime, occurring in several forms, of which only the opaque white variety is useful as a pigment.

The native mineral is quarried, dressed, ground, and levigated, in all which operations there is nothing special to be noted.

Whether obtained in this way, or prepared artificially, or formed as a bye product in other industries, gypsum affords a permanent and neutral white pigment, mixing well with oil or water, and possessing a covering power which ranks between white lead and zinc white. It has a bluish tint, but less so than ordinary white lead.

**KAOLIN.**—One of the names applied to china clay, see p. 172.

**LEAD WHITES, OR WHITE LEADS.**—On the grounds of the quantity in which it is produced and the extent to which it is applied, probably no pigment can compare with white lead, including in that term the various white pigments having lead as a basis.

In its commonest form white lead is lead carbonate. There are many ways in which it is made commercially, all dependent upon certain chemical reactions.

When a solution of normal plumbic acetate is attacked by carbonic acid, no precipitate is produced. That normal solution is formed by the action of acetic acid or hydric

acetate upon oxide of lead. It consists of a certain weight of lead to a certain weight of acid, which converts it into the acetate. Carbonic acid has no power to separate out from it the lead, and form carbonate of lead. But this acetate of lead has the power of dissolving a considerable quantity of oxide of lead in addition to that which was used in its first formation, and when this additional quantity of oxide of lead is dissolved by the acetate, a substance is formed which is termed a basic acetate, that means an acetate which contains more of the base (the lead oxide) than the normal acetate itself does. From such a solution we are able to precipitate, by means of carbonic acid, a white substance, which white substance is a carbonate of lead.

Thénard, a French chemist, proposed to make white lead in this way, but it was found that although the colour was pure and good, yet the lead had not sufficient body to satisfy the wishes of artists and painters. White lead has been made for years past according to what is called the Dutch method. Lead is cast into plates, and these plates, in some factories, are rolled into coils. These coils then are immersed in earthen pots; the pots are placed in a row, and a small quantity of vinegar is put into each pot. On the top of one row of pots a board is placed, and then other pots above, and so a stack is made. Between the interstices of the pots is put spent tan, or some other substance which by oxidation will evolve heat, and also carbonic acid gas. Now the heat which is evolved in oxidation of the spent tan is useful in volatilising the acid from the vinegar, and in the presence of this acetate the oxygen of the air oxidises the lead. The oxide of lead is dissolved by the acid, and the normal acetate of lead is formed. More oxide is produced, and this is dissolved by the normal acetate, and then you have basic acetate.

When substances containing carbon are oxidised, carbonic acid is the product of the oxidation when the oxygen is in excess, as in this particular case. Carbonic acid is then

formed by the oxidation of the spent tan. The carbonic acid then unites with the oxide of lead which was dissolved in the normal acetate, and a thin film of lead carbonate is formed. These thin films go on forming in succession, until at last nearly the whole of the lead is converted into carbonate, which retains the shape of the original lead. In some cases, gratings of lead are used. When the lead is converted into carbonate, it is ground in water and reduced to a fine powder, and is then made up into the sort of pigments required, either with water or with oil. This is, or rather was, an operation attended with considerable danger to the workmen, who were subjected to what is termed lead-poisoning, to which, unfortunately, many painters, from want of cleanly habits, are subject now.

*Dutch Process.*—In the words of Mr. Carter Bell, who has read a most interesting paper on the subject before the Society of Chemical Industry, the manufacture of white lead is a most ancient proceeding, and has been pursued with but little variation in the mode of manufacture for some hundreds of years. The Dutch seem to have been the originators of this method of making white lead, which is now so largely conducted in this and other countries.

In this process metallic lead is piled in stacks, and submitted to the action of acetic acid, watery vapour, air, and carbonic acid for some time, by which means the metallic lead becomes gradually converted into white lead.

This method is called the “stack” or Dutch process.

The construction of a stack is a very simple and rude operation. Layers of dung or tan, or a mixture of the two, are so arranged as to imbed a large number of earthenware pots, each containing some acetic acid. These pots are about 4 or 5 inches in diameter, and about 7 or 8 inches high; a coil of lead is placed in each pot, and buckles or gratings of lead supported on oaken bearers are laid across and on top of the pots; boards are laid to cover the whole, and form a floor.

The stack is composed of a number of such layers of pots, bearers, and buckles or gratings, raised one upon another.

A stack chamber is a brick enclosure 10 or 12 feet square, and 20 or 25 feet high; such a chamber will contain about 70 tons of lead when stacked and piled. In a white lead factory several of these chambers are built side by side, and when they are in full operation a set of chambers will contain as much as 700 or 1000 tons of lead.

Only the purest kind of lead will be suitable for conversion in this stack process of making white lead, the common varieties being inadmissible. Messrs. Pontifex and Wood have furnished the following analyses of lead used for white lead making.

	Copper.	Antimony.	Iron.	Spelter.	Silver.	Lead.
A	0·00700 ..	0·00490 ..	0·00200 ..	0·00080 ..	0·00100 ..	99·98430
B	0·07580 ..	0·00320 ..	0·00220 ..	0·00320 ..	0·00200 ..	99·91360
C	0·00340 ..	0·00460 ..	0·00120 ..	0·00070 ..	0·00350 ..	99·98660
D	0·05260 ..	0·00740 ..	0·00150 ..	0·00180 ..	0·00400 ..	99·93270
E	0·00940 ..	0·00210 ..	0·00160 ..	0·00100 ..	0·00075 ..	99·98515
F	0·02360 ..	0·00580 ..	0·00210 ..	0·00180 ..	0·00100 ..	99·96570

The presence of silver, copper and iron in the lead would damage the colour of the white lead resulting, and other admixtures retard or prevent the progress of conversion.

In olden times horse dung was the only imbedding material used in the stack arrangement. This material when heated evolves gases which seriously interfere with the colour of the resulting corrosion. Dung has been almost superseded in this country by tanners' refuse; in Belgium dung is yet employed, and in some places a mixture of dung and tan.

Where dung is used, the process of corrosion of the lead goes on more quickly than when tan alone is employed, but the use of tan offers great advantages, especially this one: that it does not give off gases that damage the white lead.

The operations of charging and discharging these chambers are principally the work of women, and are most laborious and fatiguing.

In emptying the chambers and stripping the stacks, the women are fully exposed to the heated gases which are yielded by the decomposing tan, and the heated and corroded lead. These gases, in themselves most injurious to health, are not to be compared in this respect to the dust which pervades the air and fills the chamber in which these women work.

When a stack is charged, the chamber containing it is enclosed. The tan or dung within soon commences heating, and the heat soon causes the acetic acid in the pots, and the water in the tan or dung, to rise in vapour and penetrate the stack. Air is admitted to the stack through openings left for that purpose, and carbonic acid is evolved from the heated decomposing tan or dung, and this gas also penetrates the stack, and the process of converting blue lead into the white lead gradually proceeds, and the blue metal becomes corroded and incrusted with a white crust or covering.

As to the exact chemical changes and combinations proceeding in the working of a stack, differences of opinion exist, but we may fairly conclude that the process resolves itself into this—first, the formation of sub-acetate of lead, which, decomposed by the agency of the carbonic acid gas, becomes reduced to the condition of normal acetate by loss of a portion of its basic oxide of lead. The reduced sub-acetate then again takes up an additional molecule of oxide of lead, and is re-converted into its original subsalt state, to be again attacked and reduced by the carbonic acid gas, and so on continually during the working of the stack. It will be evident that the “nascent” state of the various substances disengaged during the chemical changes which are proceeding in the stack is an important factor in this process, and must be taken into account in considering the philosophy of the operation.

It will also be evident that the mode of proceeding in white lead making by the stack process is most crude and

clumsy, and a most uncertain method, one governed by rule of thumb, and by no element of certainty or science. White lead makers, as a rule, know nothing of the chemistry of their subject. This absence of chemical knowledge of the subject, by those who are engaged in this manufacture, may explain the curious circumstance that for hundreds of years this industry has been pursued in the same old-fashioned and uncertain way, and the stack, or Dutch process, still holds its ground and displays little or no advance in knowledge or improvements in its method of proceeding, even in the present age of precision in almost every branch of manufacture. The uncertainty of the stack process is shown most clearly in this: That stacks may work and some do not work. In the latter case all the time and labour spent in forming the stacks, and all the acid they contained, is lost.

No amount of foresight will avail to determine beforehand which stack shall accomplish the conversion of its contained metallic lead, and which will not.

The stacks are generally allowed to remain in operation, after they are charged, three or four months; in this time it is presumed all profitable action in the stack has ceased. The temperature of the stack, which had risen gradually from the normal temperature to 100° or 150° F., will have gradually fallen, and this falling temperature is the indication that the corrosion of the lead in the stack has terminated.

After the three months' action of the stacks, they are stripped and pulled to pieces. Some will be found to be done better than others, and one part of the same stack will be done more perfectly than another. The coating on the lead will also differ; some will be smooth, regular, and equal in formation, some will be rough and blistered, and far from uniform. The rough blistered casting is rejected as unfit for white lead making: the workmen call it "dross." The smooth laminated coating is the one preserved for the after manufacture.

It is a curious fact connected with the consideration of the total want of educated guidance in these matters that prevails, that in all factories of this description some chambers are noted as always working well, and others are equally well known to always do their work the reverse of well. No one knows why! No one stays to seek the reason. The factory way goes on filling and emptying these white lead chambers whether the stacks be working well or no.

The incrustation that is most esteemed by the manufacturers of white lead in this old-fashioned style is a hard, china-like material, formed of thin deposits, layer upon layer, in a slow, continuous, regular way. It is at once conceivable that in the rough-and-ready manner of stack manufacture most irregular action must proceed.

It would be almost impossible for the contents of the pile or stack to be submitted to the same action of the gases throughout. Some parts of the stack and its contents will be under more favourable conditions than others, hence the reason why, in practice, it is invariably found that some stacks, and some parts of a stack, work better than others. Under the microscope, this good crust of white lead, the proper incrustation from which to prepare white lead, will be readily seen to consist of very thin coatings or layers of white lead, which have been slowly formed on the metallic lead and piled one upon another to the thickness of an eighth or a quarter of an inch. This formation constitutes the hard, china-like substance, which alone possesses the chemical constitution and the properties to form good white lead paint.

White lead makers, recognising this peculiar incrustation as the only one capable of fulfilling their desired purpose of making good white lead paint, do not even recognise any other as of any service for that purpose, be it good or bad. Such a material, if obtained, however good, would be outside their experience and beyond their philosophy. After the stacks have been stripped, the gratings or buckles with their

adhering coating of white lead are moistened with water and are passed through crushing rollers to separate the unconverted lead; then the crust which has been detached is ground under heavy edge runners with water.

This detached crust of white lead will vary much in colour: it will be white in some parts, yellowish or greyish in others. These discolourations arise from various causes, but they are principally caused by the contact of the moist wood and tan. The white lead is now a rough crushed material, very hard, and requiring to be ground to the finest powder. It contains, also, small fragments of blue lead which have passed the crushing rolls, and a quantity of acetate of lead. The presence of acetate of lead is always found in larger or smaller quantities, which vary with every operation, and which invariably accompany white lead produced in the stack.

To remove discolourations—to separate the fragments of metal and to dissolve out the acetate salt—much water and washing are employed. The material is ground with water under the heavy edge runner stones, it then proceeds to a series of horizontal mills, each succeeding mill set closer than its fellow, and is further and further ground to fineness with water. From these mills it runs as a milky liquid to a series of settling tanks, where it is allowed to subside, and the clear fluid is run off to waste, or into tanks to be used over again. This waste water will now contain the colouring matter removed from the incrustation, and the principal portion of the acetate of lead which the incrustation previously contained, and any other soluble matters removed from the washed and ground material. The small fragments of lead which passed the crushing roll and edge runner mills will have been previously removed by subsidence in water.

The white lead deposited in the tanks is in some factories ladled out into skips and agitated by a “dolly,” which further enables the heavy powder to get free from the water

in which it is entangled. The moist powder is next placed on trays or dishes, and is conveyed to the stove or drying chamber. Women always perform this work.

The drying or stoving room is a large enclosed space heated by a "cockle" arrangement; rough scaffoldings are erected within this chamber, on which women mount to stow the trays on shelves fitted for the purpose. The trays and their contents remain in the heated atmosphere of this chamber for two or three weeks, by which time they become dry and ready for removal, to be packed in lumps for certain markets, or ground to dry powder and packed in barrels for others.

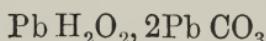
Women are employed to fill and also to empty the drying or stoving chamber, and during this work they are fully exposed to its contaminating atmosphere. Hot and dry, and charged with fine dusty particles of white lead, it becomes a dangerous trap, and contaminates the blood of those engaged with its deadly poison. It is in this part of the manufacture that the principal damage to health occurs. This is the most laborious work; heat makes it very fatiguing, the atmosphere within this chamber being always much above the exterior air.

Recent Government regulations have sought to curtail these and other evils in this manufacture. Women engaged in these stoves are ordered to wear overclothing, headdress and respirators. The general experience of their practice, notwithstanding Government regulations, is this; that they cannot work in them with ease and convenience, and more often wear the respirator around their necks than in front of nose and mouth. The excessive mortality in women who work in these stacks and stoving houses scarcely requires assertion. Few, even of those who employ them, know the extent of the deadly operation. Recently, medical men have made public that cases are within their knowledge of children born already contaminated with lead poison. Woman labour should surely be restricted by Government enactments in all such deadly occupations.

We may sum up the whole matter as regards white lead making by the stack or Dutch method in a few brief words : It is a most tedious and uncertain operation ; it is a most dangerous occupation for all concerned ; it is founded upon no true principles of any kind ; and of science its whole course is ignorant. White lead making is ruled by a "happy-go-lucky" philosophy. The representatives of this manufacture are completely ignorant of the scientific details relating to it, and hence we may not be surprised to find amongst them an enormous amount of ignorance and prejudice.

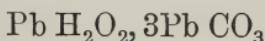
Good white lead will not differ materially in its composition by whatever process it may be made, but it may differ seriously in its physical character, and in its fitness to produce a substance adapted to the uses to which white lead paint is applied. Good white lead is a compound which contains hydrate and carbonate of the metal, in the proportions either of one molecule of hydrate of lead combined with two of carbonate, or is made up of one molecule of hydrate with three of carbonate of lead.

If we consider the first compound roughly



white lead will be made up of one part of hydrate and two parts of carbonate of lead.

The second compound roughly estimated



will be one part of hydrate, combined with three parts of carbonate or lead. The latter will be in the proportion of 75 per cent. of carbonate and 25 per cent. of hydrate of lead, and this represents the composition which has been assigned to good white lead by those most acquainted with the subject. The amount of hydrate contained in white lead should never exceed the proportion above named of 25 per cent., nor should its amount be much below the 25 per cent.

The hydrate contained in the substance serves to unite with the oil in the paint; it forms therewith a drying white and elastic varnish which embraces and holds the particles of white carbonate and prevents their subsidence and separation in the paint. There is a chemical action of a much more intimate character between the components of good white lead when mixed with oil which neither of the constituents of this compound can alone produce.

For instance, hydrate of lead and linseed oil produce a varnish-like substance, semi-transparent and of no covering capability.

Carbonate of lead and linseed oil produce a compound which is opaque, but has no body or covering power, and in which the white solid carbonate is held in feeble mechanical suspension.

Neither of them constitutes a paint, but when together as white lead they are mixed with oil, combination takes place, and serviceable paint of good body and covering power and enduring quality is produced. Good white lead is a dense, perfectly amorphous powder of perfect whiteness, possessed of great body and covering power when combined with oil. When mixed with linseed oil and used as paint it rapidly dries in the air and assumes a varnish-like, glossy, hard surface, and is capable when once dry of resisting the action of air and water for any length of time. It does not weep when laid on a surface with a brush, that is, the oil does not separate from the solid material of the paint.

Attempts have been made to produce white lead quickly and cheaply by precipitating processes, but in all such methods the resulting compound is deficient in certain special qualities absolutely necessary to white lead proper and to its uses. The precipitated white lead is always of a crystalline structure, and crystalline lead can never furnish a good body paint—no amount of pulverising and grinding of this crystalline material will correct this defect in its nature, and deprive it of its crystalline form.

“Once a crystal always a crystal” has an especial applica-

tion to this point of our philosophy. Pulverising a crystal will not alter its structure, but simply reduces the size of the crystals. Crystals of white lead are unable to effect the necessary combination with the oil and form the true varnish which white amorphous lead so readily produces. Paint made with the precipitated white lead lacks body and covering power, and this because of the absence of this chemical union with the oil.

The manufacture of white lead by process of precipitation, even were the resulting preparation suitable, does not correct the evils of the present method by Dutch or stack process of making white lead.

A solution of lead may be precipitated in a few minutes, but it cannot be made so quickly. The white lead, after its precipitation, has to be filtered or separated, washed and dried, and ground to powder, which processes cannot occupy less time than a few weeks for completion.

Precipitated white lead has been made in France and Germany for some years, and it is now manufactured in those countries. It is now made in England by one patent process, but the product lacks certain qualities, and is consequently still open to the objections already noted.

Substitutes for white lead of a non-poisonous nature, or of such a nature as not to produce such deadly effects in their preparation or use as white lead does, have been proposed; their introduction has not, however, been a great success. A mixture of sulphate, sulphide and oxide of zinc is a patent white made by subliming galena in an oxidising furnace or hearth. This compound lacks body.

All of these so-called substitutes are very inferior to white lead, not only as to quality but as to cost. They cannot compete with white lead. A committee of enquiry on these substitutes for white lead, reporting the result of their enquiry and examination, stated that they found that these were mostly prepared with varnishes before they were sold for use, and that in most instances they were mixed with a

large quantity of driers, and that the drier invariably was a compound of lead.

The principal consumption of white lead is for paint ; to produce this paint it is ground with oil in varying proportions, about 8 to 15 per cent. This produces the ordinary white lead in oil, and is worth from 19*l.* to 20*l.* a ton, but often more than this amount.

Dry powdered white lead is chiefly made for and used by grinders and mixers, who combine with it a variety of other cheaper materials—chalk, clay, sulphate of lime, and sulphate of baryta, but principal use is made of chalk and barytes. These are mixed with the white lead, and then the mixture is ground with oil and formed into paint, sold under various names according to quality : thus—guaranteed white lead, firsts, seconds, thirds, and fourths, the proportion of white lead diminishing, and that of the adulterant increasing, as we descend from the pure material. Guaranteed and best white lead is not pure, and does not mean pure white lead. Pure white lead can be purchased at some makers, but its price, if pure, can never fall below 19*l.* or 20*l.* per ton.

To sophisticate white lead, and produce the various inferiors named, dry powdered white lead is needed as a starting point, and for this purpose principally arises the necessity for its production. If ground in oil the adulterants cannot be properly incorporated with it. Dry white lead is used for nothing else that could ever give rise to any great demand for it. We have already observed that the production of this dry and powdered white lead is the most dangerous proceeding connected with this industry. Grinding in oil is unattended with any important consequence to the health and comfort of those employed. A serious drawback to the “stack” production, the china-like incrustation to which reference has already been made, is that it requires crushing, grinding, washing, and drying, and a second course of dry grinding after it is dried—the most objectionable step in its preparation.

Could the corrosion of the blue lead be effected in such a way as to prevent any discoloration of the material by the tan and wood—could the corrosion be so produced as to be easily separated from the buckle or grating on which it has formed—could this separation be so effected as to prevent the breaking up of the lead skeleton, and the presence of small pieces of metal in the detached crust of white lead, two principal reasons for washing and drying are removed.

There is yet another consideration, that is, the presence of acetate of lead, always found in varying quantities in the incrustation produced, and remaining at the close of the operation and conversion. To remove this, careful washing, and after-stoving and drying must be accomplished. The amount of this salt present is found to differ with each operation, and in various portions of the same make.

The washing out of the acetate is never perfect, and it involves a large amount of labour.

Opinions differ as to the effect of this acetate if allowed to remain in the product. White lead makers on the "stack" principle aver that it should and must be washed out, lest it should damage the qualities of the paint. This is questionable, and not one can produce practical evidence of its being the cause of any damage if still contained in white lead. Facts seem to deny its harmfulness in this respect, inasmuch as the best prepared samples, those washed and dried from the most careful makers, will be found upon analysis to contain more or less of acetate of lead.

A large proportion of this salt in white lead may not be beneficial for many reasons, but a small percentage can do no harm ; nay, for many purposes it may be good.

There is no substance used for driers for white lead that is more esteemed than this acetate of lead, commonly known as "sugar of lead."

A small amount of this salt present in white lead would communicate drying properties, and this alone is what it could do.

Granting that we can discover a method of producing white lead of amorphous character, of good density, free from all discoloration, free from all particles of metallic lead, and free from all but a small percentage of acetate of lead, then washing will not be needed.

Stoving and drying become unnecessary. The work of women, their deadly occupation, so burdensome to the operatives and to all with whom they are concerned, is done away with.

*Condy's Process.*—An improvement in the manufacture of white lead was patented by Condy, of Battersea, in 1881, which, though giving perfectly satisfactory results when carefully conducted, necessitated special precautions, and led to his substituting in practice the following additions and modifications, which are of great consequence in rendering the process more certain in the quality of its product, and more valuable as a commercial manufacture on the practical scale, by virtue of its offering greatly increased facility and economy in production.

The results of numerous and repeated experiments on the larger scale induced Condy to qualify the recommendation contained in his first patent, viz. that of employing a solution of tribasic acetate of lead and bicarbonate of soda in proper proportion to precipitate nearly the whole of the lead, and further stating that he preferred to employ "a slight excess of tribasic lead salt rather than find carbonate of soda in excess." Though, when carefully conducted, if the greatest nicety is observed, a satisfactory result is obtained; in practice, the least variation from the exact composition of the two substances is attended with the drawback that the white lead is liable to a slight uncertainty of tint after it is ground in oil, whereas by the process hereinafter described a positive and reliable result can be obtained, as the white lead produced will be of a uniform white colour, and not liable to turn when ground in oil. Though the earlier process was in itself complete for the manufacture of white lead from oxide

of lead, it afterwards occurred to Condy that a great object would be attained in rendering the process more valuable and more practical, if a method were devised, worked out, and described for the manufacture of tribasic acetate of lead to be made entirely from metallic lead by the action of acetic acid or neutral acetate of lead on metallic lead, and not to be dependent on the employment in any way of previously manufactured oxide of lead.

This portion of Condy's invention relating to the manufacture of tribasic acetate of lead may be described as follows: he melts, and, after skimming carefully, feathers the metallic lead by dropping it into water; he places this granulated lead in wooden vessels or vats previously fitted with perforated false bottoms under which are fixed taps for drawing the liquor off into other vats or tanks placed on a lower level. Having filled with granulated lead the vessels fitted with the false bottoms, he fills up the interstices with a dilute acetic acid composed of one part, by weight, of acid (specific gravity 1·045 at 60° F.) and 12½ parts of water, and after allowing the dilute acid to stand for two hours, draws it off through the taps into the lower tanks. This allows access of atmospheric air to the lead, which has the effect of heating the lead so that oxidation takes place.

After a time (about three or four hours), this oxidation begins to slacken, when he pumps up a second time the acid solution from the lower vat on to the granulated lead, and allows them to stand in contact for one hour; he then again draws off the liquid into the lower tank, and again exposes the metallic lead to atmospheric oxidation, allowing three or four hours for the latter operation; and if the solution of lead has not already attained the specific gravity of 1·040, at 60° F., he again repasses the liquor over the metallic lead partially oxidised, until it has attained that specific gravity, when he places the dissolved lead with fresh granulated lead and recommences the manufacture in the same way.

This operation succeeds much better on the large scale

than on a laboratory scale. In vats containing upwards of one ton of lead, the result is all that can be desired, and can be obtained by passing the liquor from twice to three times over the metallic lead partially oxidised. A little practice enables the operator so to control the process that he can obtain the solution of the desired specific gravity with perfect ease.

This plan of manufacturing tribasic acetate of lead possesses the advantage of producing that substance wholly or nearly wholly free from the impurities contained in metallic lead, such as copper and silver, which are not taken up, or soluble, in the presence of metallic lead. In consequence of the circumstance that foreign matter is left almost untouched, it is practicable to make white lead of a fine quality from old lead such as lead piping, roofing, and worn out lead generally, which can thus be utilised to greater advantage than in any other way.

Having obtained this solution of basic acetate of lead of the specific gravity of 1·040 at 60° F., Condy proceeds as follows:—To the solution produced by each 60 lb. of acid and 750 lb. of water previously pumped up into another vat or tank, he adds bicarbonate of soda in the proportion of 30 lb. for each 60 lb. by weight of acid originally employed, and agitates the mixture. This will generally precipitate all the white lead, but it is necessary to test the filtrate to ascertain the exact point when all the lead is thrown down. Sufficient bicarbonate of soda should be added to do this completely, and it would be better to use bicarbonate of soda in excess rather than leave any lead unprecipitated, as by this means greater certainty is obtained in securing on the large and practical scale a white lead capable of standing the effect of light and grinding in oil without changing. The white lead after precipitation can be washed, pressed, and dried in the usual way.

The following variation may be made from the method described of making tribasic acetate of lead, thus:—To each

60 lb. of acid and 750 lb. of water may be added sufficient of the tribasic solution to make neutral acetate of lead, with which to recommence the manufacture of tribasic acetate of lead by the process described. Vague reference has been made in works on technical chemistry to the possibility of using metallic lead in the manufacture of sugar of lead, but such references have been practically worthless, as they contain no information of a practical nature even for the manufacture of neutral acetate of lead, and no process at all has ever been described for the manufacture of basic acetate of lead from metallic lead acted on by acetic acid or acetate of lead.

*Gardner's Process.*—The conditions observed and fulfilled in the arrangements adopted by Prof. E. V. Gardner, are founded upon a study of the nature, properties and behaviour of the substances concerned, under certain methods of treatment.

There are several oxides of lead which may be formed under special conditions.—(1)  $Pb_2O$ , and the same oxide combined with water  $Pb_2H_2O_2$ ; (2)  $PbO$ , and the same oxide combined with water  $PbH_2O_2$ . In the hydrated form these oxides combine readily with carbonic acid, but they do not combine readily with carbonic acid when dehydrated. The hydrates are most readily formed at about  $120^{\circ}$ – $130^{\circ}$  F., and are decomposed after they are formed if heated to  $212^{\circ}$  F.

These oxides and their hydrates combine with acetic acid to form acetate and sub-acetate of lead, and with nitric acid to form nitrate and sub-nitrate of lead.

Lead, submitted to the action of air, watery vapour, and acetic or nitric acid, or a mixture of these acids, with air or oxygen, with proper precautions, forms sub-acetate or sub-nitrate of lead, and this sub-acetate or sub-nitrate of lead readily absorbs carbonic acid and forms carbonate and sub-carbonate of lead.

Sufficient acetic or nitric acid, or a mixture of these and air or oxygen, and watery vapour, must be constantly sup-

plied to form the subsalts of lead to carry on the operation of converting blue lead into white lead ; but an excess or an insufficiency of these agents will in either case prevent the formation of sub-acetate or sub-nitrate, and consequently of the sub-carbonates.

Thus—too little air, acetic acid and aqueous vapour prevents the formation of the hydrated sub-acetate and consequently sub-carbonate of lead. Too much acetic acid and aqueous vapour, and too little air forms an acetate on the surface of the lead, which, by the excess of water, dissolves and wastes, and washes the lead ; it also varnishes the surface of the lead with a coating of acetate, and checks, if it does not completely prevent, the formation of sub-acetate of lead, and consequently the formation of carbonate and sub-carbonate of lead. Similar rules hold good in the case of nitric acid and the formation of nitrate and sub-nitrate.

The process of forming the hydrated sub-acetate or sub-nitrate of lead is most energetic at a temperature of 120°–130° F. In a lower temperature, a much longer time is occupied in carrying out the process of conversion ; while at a higher temperature the delicate sub-acetate or sub-nitrate of lead first formed suffers loss of water, until, at 212° F., it is completely dehydrated. At a temperature about 135° F., the power of forming carbonate and sub-carbonates is lessened, and at 212° F. is considerably diminished. The carbonate itself is dehydrated at 212° F., and is decomposed at a higher temperature.

To obtain a white lead of excellent quality for its various uses, it is necessary to produce a substance which possesses sufficient body to cover surfaces to which it may be applied as paint, and it must possess sufficient base to combine with the oil of the paint to form a vehicle or varnish to retain and hold the body on the surface. This is found to be the case with sub-carbonate of lead, or especially with a compound constituted of two or three equivalents of carbonate of lead, with one equivalent of hydrated oxide of that metal.

Lead, to be attacked by chemical agents, should possess a clean surface. If the surface of the lead is *chemically* clean, so much the better. The surface of the lead should be extended as much as possible, and exposed to the action of the gases and vapours at a certain heat for its conversion into white lead.

If the most favourable conditions are sought, the temperature should be between 120° and 130° F.; and to carry on the chemical action most satisfactorily, the lead during its conversion should present a granular coating—that is, the coating formed by the chemical agents should be granular and not smooth and continuous in character. It should be porous, and not of a continuous varnish-like or vitreous character.

To rapidly carry on the chemical action, the chemical agents should be well diffused and commingled throughout each other, and the blue lead should be so exposed as to be open to their attack on all parts of its surface equally, and all should be at, and kept at, a proper temperature and a proper degree of humidity. Too dry a heat prevents the process of conversion. Too moist an atmosphere wastes the materials and arrests their action. The conditions, therefore, which are most favourable will be a certain humid atmosphere of well diffused and commingled vapours or gases, acting on metallic lead exposed to them under the physical conditions described, and at a temperature between 110° and 135° F.

These favourable conditions can be further augmented by certain electrical arrangements in connection with them.

Again, in the sources from which the carbonic acid is derived, and in the arrangement of the apparatus for applying the carbonic acid, favourable and unfavourable conditions can be imported. Thus, by using paraffin, petroleum, benzine, or light oil of paraffin or petroleum, or similar carbonaceous substances free from sulphur, or mixtures of such carbonaceous substances either alone or mixed with air or

other oxidising substance, comparatively pure carbonic acid may be furnished without at the same time producing any objectionable compounds.

As a result of his researches and experiments, Prof. Gardner has proposed (Eng. Pat. 1882, No. 731) certain improvements in the method of converting blue lead into white lead, in the apparatus employed, and in the method of making and applying the carbonic acid used in the process. Some of these improvements are applicable to the open stack or chamber process, while others relate to closed chambers.

Preferably, for the conversion of blue lead into white lead, Prof. Gardner adopts a closed, but not air-tight, chamber. This chamber is ventilated or relieved so as to enable the incoming gases and vapours to enter it without hindrance, and to escape by means of an exit valve and pipe, or an exit shaft, connected with the chamber, communicating with the exterior air, and regulated by a valve or damper. The gases and vapours within the chamber can find their way out by this exit shaft only, by slight pressure on expansion from within the chamber; thus the interior of the chamber is preserved from disturbance, by preventing the formation of currents within its atmosphere, and yet a perfect circulation of the gases and vapours is kept up.

To warm the interior of this chamber, which is constructed of any material that will resist the action of the vapours and gases, and which is not too absorbent; Prof. Gardner makes the bottom of the chamber of such a shape as to form a heating vessel to hold water or steam, this water or steam, or both, being kept at the required temperature by means of a steam coil. Matters are so arranged that the contents of this coil are protected from any excess of pressure, and consequently the temperature seldom or never exceeds about 212° F., unless for any special reason it is desired to raise it to a higher point. Sometimes the sides are constructed similarly to the bottom.

The materials of which these chambers are constructed

must be capable of resisting the heated and acidified vapours within them. Cast or wrought iron faced with glass, slate, tiles, pewter, or glazed bricks; tinned copper, tinned brass, or pewter; timber, whether green or after carbonising by heat or sulphuric acid; all are more or less suitable. Means of observing the progress of the conversion, and means of lifting the contents in or out, must also be provided, as well as thermometers to indicate the temperature prevailing inside.

The gases and vapours which effect the conversion of the blue lead into white lead are generated outside the chamber just described, and are conducted into it by means of pipes, being first raised to such a temperature in excess of that which should exist inside the converting chamber as to allow for the cooling effect arising from the friction and loss of heat in passing through the various pipes and distributors attached to the converting chamber.

Owing to this extra heating, the gases and vapours are expanded, diffused, and commingled, and do not rob the interior of the converting chamber of any heat on entering it, so that the heat inside the converting chamber is kept constant, and can operate to further expand and diffuse the gases and vapours in contact with the blue lead inside the chamber. In practice it is found that the temperature of the converting chamber cannot be suitably controlled if any portion of the gases or vapours be generated within that chamber.

The blue lead is arranged in the converting chamber in trays, or on shelves or frames, so as to allow it to be completely surrounded and attacked by the vapours or gases, and thereby be converted into white lead, at the same time preventing the formation of direct currents or eddies. Framed supports resembling a dinner waggon serve well for holding the lead, and may easily be arranged to lift bodily in and out of the chamber with their burden of blue or white lead. The surface on which the blue lead is directly supported is

made of graphitic carbon, hard coke, platinum, or carbonised or platinised material, such as is used for plates in electric batteries, or of other material standing in a similar electrical relationship to lead, or capable of generating with it an electric current.

In applying this development of electrical energy to the ordinary "stack," as for instance the Dutch process, the pots containing the acetous liquid and blue lead are made of, or lined with, such electrical carbon, or contain a portion of it in suspension, by which the same effect is realised. Advantage may also be derived from furnishing a supplementary supply of carbonic acid to the stack beyond that due to the decomposing dung, &c.; as well as from injecting a current of air or oxygen at suitable temperatures, and from the admission of steam in a coil throughout the stack.

The generation or production of the acetic or nitric acid vapours is attained by heat in a vessel so arranged that its contents are kept at a certain temperature for vaporising, by having the boiling acid solution at about 1·003 sp. gr., procured by mixing water with vinegar or acetic or nitric acids.

The supply pipes conveying the air or oxygen and the carbonic acid, or either of them, can easily be made to emit their contents close to the boiling acid solution, whereby the vapours arising from the latter are mixed and intermingled with them, and all pass together through the pipes and distributors into the converting chamber or stack.

In preparing the carbonic acid it is necessary to observe certain precautions, especially that it shall be pure and that no carbonic oxide shall gain admission to the chamber. If the ordinary chalk and carbon method be employed, the furnace must be provided at the uptake with a series of air inlets, so as to ensure that the gases passing from the furnace to the delivery tube shall be most thoroughly oxidised.

The purification of the carbonic acid may be effected in the usual way by passing it through a vessel containing

water ; or, if requisite, it may be cleansed, expanded, and heated in one operation by passing it through or over hot water, or over a hot aqueous solution of carbonate of soda, all of which, however, incur considerable cost in plant and manipulation.

Owing to these difficulties in purifying carbonic acid, Prof. Gardner prefers to prepare a practically pure carbonic acid in the first place, and this he does by allowing petroleum, benzine, paraffin, or other hydrocarbon or carbonaceous liquid to gradually fall into a retort containing chalk or other suitable carbonate at a high temperature, whereby relatively pure carbonic acid gas is generated ; and while still in a highly heated state it encounters a stream of air or oxygen, ensuring its complete combustion before entering the converting chamber.

Another method of procuring fairly pure carbonic acid is by the combustion and oxidation of any of the liquid hydrocarbons mentioned above, in suitable lamps ; and when carbonic acid gas of exceptional purity is required, it may be obtained by heating bicarbonates to a sufficient degree to drive off one molecule of carbonic acid, reducing the bi-carbonate to carbonate, from which it can be reproduced by treatment with carbonic acid gas obtained from cheaper sources.

The *modus operandi* adopted by Prof. Gardner is as follows : The lead is granulated and prepared for conversion in one operation, thus—an iron or a slate slab about 2-3 inches thick is placed in a tank containing acetic or nitric acid solutions rising about 3 inches above the upper surface of the slab. The lead is melted at low red heat and poured from a height of 4 to 6 feet into the acid solution, through which it falls till it encounters the slab, and thereupon passes away into the surrounding solution, being thus converted into a spongy condition. In this condition the lead is spread on frames or trays, which are then lifted bodily into their places in the converting chambers. The latter

is closed and heated to 120° F. for 3–4 hours, or until the whole contents have assumed a uniform temperature. Thereupon the acid vapours and air are admitted and distributed, taking care that the temperature is not thereby reduced below 110° F. nor increased above 125° F., steam being temporarily shut off if necessary. This treatment is continued for 24 hours.

The admission of aqueous vapour should be so regulated that while a dry atmosphere is avoided, yet there is no appreciable condensation of moisture in the chamber. While ensuring this condition, the temperature may reach as high as 130° F. for a second period of 24 hours, but must not overstep the limits of 120° F. minimum and 135° F. maximum.

After 48 hours' treatment, the supply of duly warmed carbonic acid gas is admitted for a period of two hours, without discontinuing the introduction of acid vapours, air and steam; and this addition of carbonating gas is repeated for two hours at a time with intervals of four hours during which it is cut off. When, after four or five days, efflorescence or exfoliation appears on the lead, the supply of carbonic gas is increased to two hours in every four, or four in every six; and the admission of acid vapours, air and steam may also be augmented so long as the temperature is not allowed to exceed 130°–135° F. The whole operation is completed in seven to fourteen days.

Of this process, Mr. Carter Bell, in his paper before referred to, speaks in the highest terms. No washing or drying is necessary. No women are engaged in the manufacture, and but few men. The white lead thus produced by the aid of electricity is deposited in a peculiar state of disintegration, it is perfectly amorphous and non-crystalline, of the purest quality; its density is 5·8. When ground in oil and made into paint, it possesses great body and a covering power inferior to no other paint, if not superior to them all.

Painters who have used the paint, practical men, and

amongst these we may observe coach painters, have pronounced its excellence and superiority to the best ordinary white lead paint.

By this electrical process of manufacture, not only is the time consumed in the making and in the preparation of this material greatly shortened, but the cost of preparation is reduced, and added to this is the important fact, the vital factor in our consideration. The labour of women is unnecessary. No lives are sacrificed to its working requirements.

Prof. E. V. Gardner, who has been for some years occupying his attention with the subject of white lead making, with a view especially to remedying its existing evils, has invented his electrical chamber process of manufacture, and an entirely new course of after treatment. He has for the last seven or eight years been more or less occupied perfecting his conception, and accommodating it to practical and commercial claims.

Chamber processes are not new, there have been several patents enrolled for making white lead in closed chambers, but none has proved commercially convenient or practically successful in its adaptation, and none has survived to the present time.

In Germany, white lead is made in chambers at the present day. The lead in gratings or sheets is supported on wooden rods, saddle fashion, the chamber is then filled, and its contents are submitted to currents of acetic acid vapour, air, steam, and carbonic acid gas; the time needful for conversion is six or seven weeks. The after steps in the separation of the incrustation, and its preparation for trade purposes are much the same as in the "stack" product preparation. It is washed, stoved, dried, and ground. The white lead made on the German plan does not differ in any material degree, save it be in price, from the best English commodity. We may assume that the washing and drying in Germany consumes a like period of time to that process in English works, viz. two or three weeks. We then see

that the German plan of making white lead cannot be perfected in less than eight or ten weeks' time from the commencement of the corroding action in the chamber. To compare these facts and the efficiency of the different plans described :—

The time required to complete the corrosion in the stack is at least 14 or 16 weeks.

The Gardner's electric process requires for the same purpose only 14 days.

As to point of time, the German plan excels the stack, and can be carried out in one-half the time required in the stack method of conversion.

The Gardner's electrical method excels the German, and can be perfected in one-third the time needed for the German chamber operation, and one-sixth the time required by the stack.

These figures open out a most important matter when we regard the capital invested and lying dormant in stack lead works.

It is well known that we have in electricity a most powerful agent by which to effect the chemical combination of various substances on the one hand, or on the other, by its means to break up and disrupt a chemical compound. Professor Gardner's main principle of action in his new process is founded upon these facts, and he takes advantage of electrical power to cause the combination of the lead with the necessary elements to build up white lead in his chambers. He either employs electrical discharges to energise and render active in their chemical affinities the various materials engaged, or he so disposes of them as to form an electric or galvanic combination in the chamber. In the latter arrangement the chamber and its contents represent a gas battery on an extensive scale. In practice he prefers the latter plan; it is more simple, more manageable in the hands of the ordinary workmen. The original plan was to have graphite or graphitic carbon plates

or supports for the buckles or gratings of lead within the converting chamber. These carbon plates and the lead to be converted, were so placed as to form a collection of galvanic "couples" or "pairs," and in this condition were submitted to the gases entering the chamber from without. It will be understood that various modes of arrangement would occur without departing from the principle concerned.

In practice this method answered very well, but presently a difficulty arose ; not only were the graphitic carbon or graphitic plates expensive, but they were easily broken, and became friable in use. Carbon plates of an especial kind were manufactured to meet these failures and remedy these defects, not without success, but still open to objection. In looking round for some substitute to replace the carbon, two points were to be kept in view, to seek some electro-negative to lead like the carbon, and some electro-conductive like it, and some material that would bear rough handling such as workmen give, and be practically convenient in its adaptation to a working chamber.

Gold or platinum would excel in these particulars, but there are considerations which debar their use. Pure tin presented itself, and tin was tried with great success. Tin would at first be thought, on account of its close electrical relationship to lead, far from favourable to the purpose. Graphite or carbon would appear far more suitable. Practice pronounced the tin to act as efficiently as carbon. This may at first seem contradictory and strange, but if we consider that while the carbon is certainly more highly electro-negative to lead than tin, yet the tin is the more conductive, and offers the less resistance to the electric current of the two ; in this manner the tin compensates by its conductive power all it may lack, as compared with carbon, in electrical energy when coupled up with lead.

Tin plate is now used as the electric-negative element in the chamber of the Gardner plan. Tin plate means pure tin. Ingot tin is rolled out into plates, the bottom of the chamber

is covered with this pure tin plate, so are the bearers and the shelves, or supports which are to hold the lead during its conversion. Tin pipes and tin fittings, which resist the action of acetic acid, are also used to conduct the gases to the chamber to carry on the converting operation, and to preserve the product from any source of discolouration.

When a chamber is prepared for the converting operation, the whole of the lead it contains will be in metallic communication with the tin supports, and these with the tin covered bottom of the chamber.

The chamber when working is kept at a certain temperature by a steam coil beneath the floor of the chamber. The process is simple. The lead buckles or gratings are placed on tin-covered stands, somewhat in form and make like a dinner-waggon. The whole is hauled up and dipped into a bath of acetic acid and acetate of lead; it there remains for one or two minutes, it is then hauled out, drained and lifted bodily through the top into the chamber. Other stands filled with buckles are so dipped and so placed till the space of the chamber is fully occupied.

This dipping cleanses the surface of the metal, and when it is exposed to the air it is speedily coated with a hydrated oxide of lead. This is the first step in the process of conversion. The chamber when filled is closed, and its temperature is brought to about 100° F.; then vapour of acetic acid and vapour of water and air are supplied from without to the interior of the chamber. This is continued for 15 or 20 hours. The lead buckles within the chamber will now possess a whitish coating, consisting of subhydrate and subacetate of lead, and they will present a uniform colour. Carbonic acid generated in any convenient manner is next passed into the acid generator; it mixes with the other gases and vapours, and with them goes on its way to supply the chamber. Speedily the action of the carbonic acid is observed, the surface lead becomes quite white and presents the appearance of a snow shower having fallen within the chamber. The formation of

white lead is now speedily effected. This treatment is continued throughout the space of 13 days; at the end of this time the supply of acetic acid vapour is stopped, and the supply of air, steam and carbonic acid is continued, according as it is desired to obtain white lead rich in oxide or in carbonate.

After a short further period, steam and air only are sent into the chamber, which is varied in temperature to 120° or 130° F., and lastly the steam supply is stopped; air alone enters the chamber, which is kept heated by the coils beneath the floor. The contents of the chamber are now in a dry state, and the operation is terminated.

It will occur to most readers that these terminal proceedings amount in effect to a convenient method of washing and drying the white lead while it is still attached to the parent lead, and this it is in fact.

The contents of the converting chamber are lifted out through the opened top, and the buckles or gratings with their crust of white lead are turned into the agitator. This agitator is an iron cage revolving inside a closed chamber of the same material. During the revolution of this cylinder or cage, the contained lead gratings fall from side to side, and the incrustation on their surfaces becomes detached and broken up. It falls in this broken state through the bars of the cage or cylinder into a receptacle beneath. The denuded buckles or gratings are retained in the cylinder and are removed. These gratings or buckles are cast of such a thickness as to withstand two or three converting operations in the chamber before they are recast.

This crude white lead is carried by an elevator, or it falls into the hopper of a pair of granite crushing rolls, also enclosed; and from these it passes into the mixer or incorporator from which it can be removed in a dry state or mixed with oil.

The incrustation of white lead will be found upon examination to be possessed of some peculiarities, the result of

the electrical action which has been going on within the chamber. It is quite white. It falls from the lead buckle or grating which it coats, if the grating be struck against a piece of wood with but a slight blow. It is easily friable, and can be rubbed to the finest powder between the thumb and finger, or on the palm of the hand.

Now, we may explain, as we conceive it, the philosophy of its production in this state of disintegration.

We know that a feeble and prolonged current of electricity will in time deposit metals from their solutions in a crystalline condition, and that if we quicken the current of electricity and cause it more energetically to act on the same solution, we can precipitate the metal from that solution in a state of powder.

It is to similar action of electricity as that to which we last refer that we ascribe the formation of the crust on the gratings of lead in the non-adherent and disintegrated condition in which it is produced, and by reason of which it is so easily detached from the lead and broken up to powder. No edge runner grinding, such as is required by the stack process, is in this case necessary.

The crude white lead and crushed material, whether in a dry state, or incorporated with oil, is finished and ground in a granite roller paint mill, from which it issues as dry white lead, or as white lead in oil.

Paint made from this electric white lead has been sent to America, to France, to Belgium, to Germany for trial, and has also been largely tested in this country by painters, engineers, and others unacquainted with its precise nature, and it has been productive of good results.

Of its density, body, and covering power, there can be no doubt, and never once have these qualities been called in question.

The cost of the manufacture of white lead by the stack process is about 3*l.* to 3*l.* 10*s.* per ton. By the German method, the cost is about the same as by the stack. By

Gardner's electric process, the cost of conversion is 10*s.* a ton. To this 10*s.* must be added the cost of labour expended in preparation, an item which cannot be well estimated on the present limited scale of manufacture; it could not exceed an additional 15*s.* a ton. This would bring the cost of manufacture of electric white lead to 25*s.* a ton.

In this electric process inferior lead can be operated upon with success. Brands of that metal such as white lead makers by the stack method dare not employ, may be successfully converted in an electric chamber, and with fair results as to the quantity and quality of the white lead produced.

By the use of Gardner's electric process it would appear that we not only preserve health, but save lives; we not only save time, but interest on large capitals, which lie idle for long periods at a time; and we can economise and simplify the whole manufacture and preparation of white lead, divesting it of all its present cumbersome and unhealthy stages. Gardner's process, we believe, must take a prominent position as one of the most necessary, valuable, and scientific inventions of modern times.

*Hannay's Process.*—Mr. J. B. Hannay, whose name is well known in connection with various chemical and engineering inventions and processes, has recently brought out a process for the manufacture of white lead. The old method of producing white lead or carbonate of lead is one involving much time and labour, together with no small risk to the health of the workpeople. By the new process brought out by Mr. Hannay, sulphate of lead is manufactured direct from galena or lead ore, without the necessity of the intermediate process of the reduction of the ore and the extraction of metallic lead. It is said that the sulphate of lead produced by the new process is whiter and more permanent than the carbonate.

The process is described as follows:—A furnace, 36 in. by 30 in., and 48 in. deep, contracting to a narrow chamber

about 36 in. long by 14 in. wide, communicating with the main flue, is charged with coke and brought to a red heat. The bed of coke is so thick as to be almost up to the level of the sill of the furnace door. The lead ore is not charged in large quantity and left for an indefinite time, but is thrown in in quantities of a few shovelfuls at a time, the object being to effect extremely rapid volatilisation and consequent oxidation. The proportion of ore to fuel is 1 ton to 1 ton, and the result is said to be the conversion of 95 per cent. of the charge into its equivalent in white lead. In the first or wide chamber, the coke is oxidised, carbonic oxide being the resulting gas, the rapid volatilisation of the galena or sulphide of lead also taking place in the same chamber. On entering the inner portion of the furnace, the volatilised sulphide of lead and the carbonic oxide are converted into carbonic acid and sulphate of lead.

Forced blast has been employed to cause the high temperature necessary for the volatilisation of the ore; but it has been found unnecessary, admission of air at atmospheric pressure through tuyere holes being quite adequate. After leaving the inner chamber of the furnace, the gases pass into a flue, level with the furnace, and about 40 feet long by 16 square feet in sectional area. From this flue the gases pass into a tower about 20 feet high, and from thence into wrought-iron flues 3 feet in diameter. These flues terminate in a wrought-iron chest, in which are fitted two steam injectors. The gases are forced by these injectors into the central chambers of the condensers. These condensers are two in number, and contain a central chamber, 16 feet by 12 inches, into which the gases are forced as described. The gases escape through interstices into the outer chambers of the condenser, and are there condensed, a continuous stream of water occupying the lower part of the condenser. The waste gases escape by a downcast leading to a tall chimney. The temperature of the gases as they enter the condenser is about 840° F.

The product is pumped from the condensers to a settling vat. Here it settles for an hour, the deposit being pumped into a second vat and washed with dilute sulphuric acid, in order to remove impurities. The resulting product is washed several times with water, and is then passed through a filter press. From the press it drops into bogies, which carry the pulp to the drying house, where it is dried by hot air. The process would thus appear an extremely simple and practical one. Several chemical authorities of repute, as well as manufacturing firms and others who have used the new white lead, have expressed themselves strongly as to its merits. One point immensely in favour of sulphate of lead as opposed to carbonate, is that the former is almost entirely innocuous, whereas the poisonous properties of the other are well known. It is claimed that the sulphate is not acted upon by coal gas or by the atmosphere of towns, which is always more or less impregnated with gases such as sulphuretted hydrogen, whose reactions with various metals have only too good reason to be known.

According to the patent specification bearing the names of French and Hannay, they employ lead ores, lead fume, or lead slags containing sulphur; and when these materials do not contain sufficient sulphur to form a sulphate with all the lead which sublimes in the process, they add to them pyrites or other sulphur-yielding substance to make up the deficiency. They heat the materials mixed with a suitable proportion of coke in an air-blast cupola furnace, which is by preference of an improved and special construction shown in Figs. 18 to 20, and hereinafter described; and they thereby produce sulphite of lead as a sublimate, provided that there are no chlorides such as common salt present in the charge, in which case sulphate and chloride of lead will be formed.

The sublimate is carried forward with the current of gases through flues to a fume condenser, which is by preference of the kind known as Wilson's and French's. As the gases and sublimate pass through the flues, hydrochloric acid is mixed

Fig. 18.

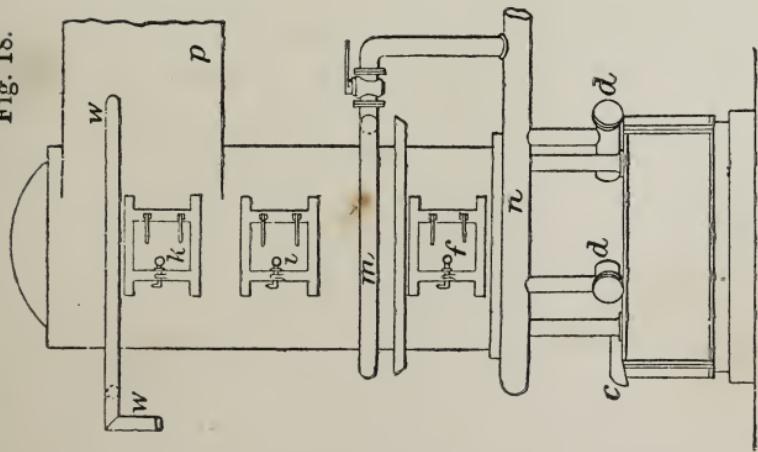


Fig. 19.

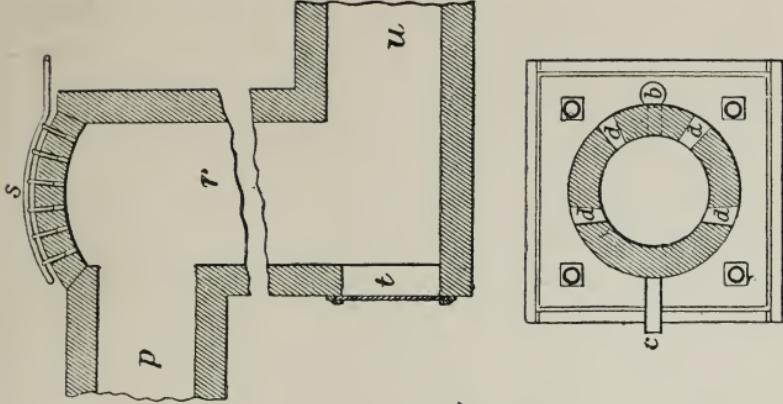
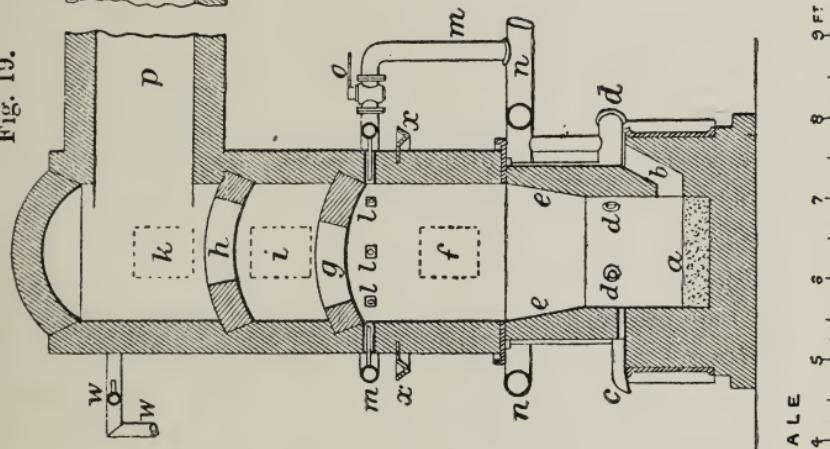
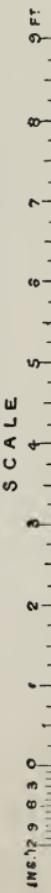


Fig. 20.



FRENCH AND HANNAY'S WHITE-LEAD FURNACE.

with them, being by preference formed in a chamber in connection with the flue, by introducing a solution of chloride of sodium in spray, and by providing a sufficient excess of sulphurous acid beyond that required for forming the sulphite of lead. Air is also present, and a well known reaction takes place, yielding hydrochloric acid and sulphate of soda, the operation taking place at a part of the flue near enough to the furnace to be always at a red heat. The hydrochloric acid thus mixed with the gases and sublimate causes the formation of chloro-sulphite of lead, or other combinations of lead, sulphur, oxygen, and chlorine of variable constitution, depending on the proportions of the several constituents, but in most cases the product is a body which forms a white pigment of extremely good quality.

Fig. 18 is an elevation of their improved cupola furnace ; Fig. 19 is a corresponding vertical section ; and Fig. 20 is a horizontal section as at the level of the principal tuyeres.

This cupola furnace is formed with a deep hearth *a* (like the American lead smelting cupola) having a siphon outlet *b*, for withdrawing molten lead when necessary. At a level a little above the siphon outlet *b*, an outlet *c* for slag and scoria is provided, and the main blast tuyeres *d* enter at about the same or a slightly higher level. With this arrangement, a considerable depth of melted lead is constantly maintained, and the choking of materials is thereby avoided at the level of the tuyeres. For a short distance above the main tuyeres *d*, the interior of the furnace is made with the sides *e* moderately and gradually widening upwards, and is afterwards continued upwards of uniform diameter or width. The charging door *f* is between 3 and 4 feet above the main tuyeres *d*, and the space above the charging door is crossed by two or more arched diaphragms *g h*, of brickwork, having irregular openings in them, there being doors *i k* in the side of the furnace above each diaphragm, for inspection and cleaning. The purpose of these diaphragms is to cause the air, gases, and sublimate to become thoroughly intermixed and

to ensure the complete combustion of any black smoke and the oxidation of any sulphide of lead that may be present.

An upper series of small tuyeres or jet pipes *l* is provided for admitting air a little below the lowest diaphragm *g*, these jet pipes *l* being supplied by a branch pipe *m* from the main air blast pipe *n*, it being found that the introduction of the air and the production of heat can be best regulated by supplying a portion at the upper part of the furnace in this way, in addition to that supplied by the main tuyeres *d*; and a tap or valve *o* is fitted on the branch pipe *m* for adjusting the supplementary supply thus admitted. Above the highest perforated diaphragm *h*, the interior of the furnace communicates with a lateral flue *p*, through which the gases and sublimate pass; and at a part of this flue *p*, sufficiently near the surface for the gases to be still hot enough, an enlargement or chamber *r* forming a descending part of the flue, is constructed. Into this chamber *r* a solution of chloride of sodium is introduced as a spray from a number of jet pipes *s*, for the purpose hereinbefore explained. This chamber *r* is provided with a door *t* at its lower part, for periodically removing matters that become deposited in it. The continuation *u* of the flue communicates with the lower part of the chamber *r*.

Preferably the spray of chloride of sodium is fine enough to allow of all or nearly all of the water being instantly evaporated, so as to leave the salt in fine particles, and in a favourable condition for being acted upon by the sulphurous acid, steam, and oxygen present in the gaseous currents. The temperature of the chamber *r* should not be allowed to fall below red heat. The proportion of chloride of sodium used will depend on the amount of chlorination of the lead that may be desired, in addition to what is necessary for converting the zinc and other metals into chlorides. In practice a proportion of salt  $2\frac{1}{2}$  to 5 per cent. of the weight of the sublimate formed answers the purpose and yields a good product, but a larger proportion may be used without injury.

It is of great importance to keep the temperature of the upper part of the furnace steadily at a red heat and flaming, as the colour of the sublimate will be inferior if the temperature is either too high or too low. To facilitate the proper regulation of the temperature, a pyrometer (which may be similar to the kind used in ironworks) is employed, which pyrometer is placed in the flue at a distance from the furnace where it cannot be injured; and by a few trials is ascertained what temperature should be indicated by the pyrometer when the temperature in the furnace is what it should be. This point having been ascertained, a glance at the pyrometer will at any time show whether the furnace is working properly or not. The inventors also provide for rapidly cooling the upper part of the furnace without interfering with the lower part, in the event of the heat becoming too great, by arranging a water pipe *w*, with a set of jets, round the top of the furnace, so that on turning a tap on the supply pipe a spray of water may be applied to the outside of the furnace; and as it is desirable that water applied in this way should not run down to the lower part of the furnace they build gutter plates *x* into the sides of the furnace just above the charging door *f*, to lead off any surplus water to a drain pipe.

Sufficient hydrochloric acid may be formed or introduced, as hereinbefore described, not only for forming chloro-sulphite of lead in the condenser, but also for saturating all the free oxide of lead, and for combining with and rendering soluble any iron, zinc, antimony, silver, or other metals. The chlorides thus formed become dissolved in the water of the condenser, and the solution, separated from the insoluble white pigment, may be treated by known processes for recovery of the metals. When the lead ores or other lead-yielding materials contain silver to a greater extent than 5 oz. per ton, a notable quantity of the silver is volatilised, and if it is left in the white pigment it renders the latter sensitive to sunlight; whereas if rendered soluble in the

manner hereinbefore described, and separated by any of the known processes, it becomes a source of profit.

The white pigment is washed in the ordinary way ; and when chloride of zinc is not completely removed by washing, a small quantity of sulphuric acid may be mixed with the pigment, by adding the same to the last washing water, to convert the chloride of zinc into sulphate, which is not hygroscopic.

The white pigment made as hereinbefore described is a very good and economical material for manufacturing into chrome yellow, this being done by mixing a solution of any suitable chromate or bichromate with the wet pigment ; whilst the chrome yellow thus obtained may be converted into chrome orange or red by treating it in the usual way.

*Italian Process.*—The precise period of the introduction of white-lead manufacture in Italy is unknown, but it was certainly previous to the beginning of the present century. Prior to 1881, the Dutch process was exclusively used in Italy. In 1881 the so-called Brumlen and Dahn process was introduced into Liguria. Somewhat later the Rhenish process was introduced. The Rhenish process is one in use in nearly all the Italian white-lead manufactories. It is employed in a large manufactory at Cogoleto, as follows :—Lead in thin sheets of about 3 feet in length, and 4 inches in width are placed in a clay chamber having the form of a cube, of about the capacity of 5800 cubic feet. In this chamber there is a wooden framework, upon which are hung the sheets of lead. Three of these sheets weigh together about  $4\frac{1}{2}$  lb., and as the capacity of the chamber is about 20 tons, it can hold about 30,000 sheets of lead.

On the floor of the chamber are placed twenty-four copper receptacles, each having four circular apertures. These receptacles are all in direct communication with a large pipe of masonry, which, by means of a copper tube, receives the gas coming from a boiler and furnace placed under the chamber. In the boiler, which is also of copper, is placed a

mixture of 900 parts of water, and 80 parts of acetic acid concentrated to 40°, and the capacity of the boiler is about equivalent to 25,882 gallons. The furnace serves the purpose of producing carbonic acid.

The gaseous mixture, consisting of volatilised acetic acid, carbonic acid, and aqueous vapour, is admitted from the boiler and furnace into the chamber in quantity and proportions best adapted to each stage of the work. The chemical reactions resulting are analogous to those which take place in the Dutch process, and the Brumlen and Dahn process. Each operation lasts six weeks, and gives a product of about 20 tons of white lead, with a consumption of 7 per cent. of acetic acid, and 9 tons of coke. The residuum of lead is about 10 per cent. of the quantity placed in the chamber. At the end of each operation the white lead taken from the chamber is washed and purified in large tubs, some of which are furnished with filters. Finally, it is packed in earthen vessels, and dried, when it is ready for the market, and is sold either in cakes or powder.

The establishment at Cogoleto, above referred to, is able to produce annually about 2000 tons of white lead, of which 1200 tons are produced by the Rhenish process, and 800 tons by the Brumlen and Dahn process. There is also in a manufactory in Milan, the process of revolving heaters. The process of precipitation has not yet been used in Italy. The Rhenish process, as above described, furnishes the greater part of Italian white lead. The smaller manufacturers still use the Dutch process, but the Brumlen and Dahn process is generally regarded as unsatisfactory.

It is believed that the production of white lead in Italy during the first ten years of this century was about 300 tons per annum. The total annual production at present is, in round numbers, about 3500 tons, of which 2800 are produced in the Ligurian manufactories, and about 300 in those of Naples. Milan also produces about 300 tons.

The product finds a market almost exclusively in Italy.

The annual amount exported is about 300 tons, and goes chiefly to Constantinople. Of the quantity of 2000 tons per annum produced at Cogoleto, about 300 tons is sold mixed with oil. No exact statistics are attainable as to the total amount of Italian white lead which is annually sold other than in the dry state, but it is believed to be little, if any, larger than 300 tons.

When the price of white lead was high, sulphate of baryta was mixed with carbonate of lead to produce white lead of inferior quality, but in consequence of the present price of white lead the use of sulphate of baryta has almost entirely ceased. No other methods of adulteration are known to be in use. In Italy, white lead is universally known as "*biacca*" when it is sold in cakes. When sold in powder it is known as "*carbonato di piombo*" (carbonate of lead). The lead from which all the white lead made in Italy is manufactured comes from the lead mines of the island of Sardinia, with the exception of a very small quantity of argentiferous lead coming from Spain. The acetic acid used in the process of manufacture comes from France. The market price of white lead in Italy is now about 45 lire the quintal (equivalent to 18s. per cwt.).

*Lewis's Process.*—Many attempts have been made to substitute for carbonate of lead—the ordinary poisonous white lead, that slowly but surely induces paralysis in those who come in contact with it for any considerable period—some less deleterious pigment. Zinc white has often been put forward as a substitute, and is indeed largely employed; but it is open to the objection of not possessing sufficient body or opacity. Sulphate of lead is not poisonous; but, when prepared in the ordinary way by precipitation, is of a crystalline nature, and, therefore, wanting in both these qualities.

A sulphate of lead has, however, been produced by John T. Lewis, of Philadelphia, by sublimation, which, when treated by the Freeman process, is stated to possess a body and colour superior to the best white lead made by the

ordinary process, with the additional merit of being cheaper, while it is also non-poisonous.

In the smelting of lead ore into pig lead, 15 per cent. goes off in fumes, and 10 per cent. are all that it has hitherto been found possible to recover ; by this process, however, the whole 15 per cent. are recovered. The sulphate may also be produced from a low quality of galena, or lead ore, which is not suited for smelting into metallic lead, and from the slag formed in the process of smelting.

The plant consists of simple subliming furnaces, iron cooling pipes, suction fans, and a series of flannel or calico bags, arranged vertically in a building, well ventilated, so as to allow the filtered gases to escape, leaving behind the sublimed white lead, which is then merely shaken down from the bags into barrels placed beneath them. The manufacture is carried on at Joplin, Missouri, with four subliming furnaces, about 500 feet of cooling pipes and towers, with suction fans, which drive the fumes into 300 bags, 20 inches in diameter, and 38 feet long, arranged vertically. About 50 tons weekly of white lead are now being produced from waste fumes, slag, and poor ore, by this establishment alone, at a cost not exceeding that given in the following figures :—

	£	s.	d.
20 cwt. of galena (with 82 per cent. of ore) .. .. .	8	0	0
Cost of subliming and catching, including repairs,			
labour and all expenses .. .. .. .. ..	1	10	0
Casks .. .. .. .. .. .. .. .. ..	0	6	0
			9
			16
			0

Freeman's process (see p. 254) consists of grinding together, in a dry state, under great pressure, and consequently with great friction, sulphate of lead and sulphate of zinc. While neither of these two substances alone possesses good body or opacity, when treated by this process they are so changed in character that the new substance is stated to be superior in these respects to the best form of ordinary white lead.

The white lead thus obtained mixes well with oil, and has also the advantage of not becoming blackened when exposed to the fumes of sulphuretted hydrogen, and of not peeling off in a saline atmosphere. As a basis for coloured paints, it is recommended on the ground that, being decomposed with greater difficulty, it can be mixed with almost any colouring substance; and, being free from acid, it does not change the tints of other substances.

The details of Lewis's process, and the plant employed, are more fully set forth below.

Heretofore the manufacture of dry white lead from galena or the native sulphurets has been effected by roasting or desulphurising the galena, and then mixing the residue, after roasting, with carbon, and subjecting the mixture to the action of heat in a compound reducing or subliming and oxidising furnace, and collecting the resulting fumes in textile bags.

Lewis's process, however, is based upon the discovery that by subliming unroasted galena, or the native or raw sulphuret of lead, and then oxidising the volatile products, cooling the fumes, and collecting them by means of a textile fabric, a superior basis of a pigment can be obtained. The admixture of carbon with the raw ore will facilitate the subliming process, or it may be carried on in a muffle or reverberatory furnace without the previous admixture of carbon.

The furnace, which has been found to answer well for the purposes above mentioned, is commonly known as the Wetherill furnace, and is represented in plan, in Fig. 21; in front and back elevations, in Figs. 22, 23; and in central longitudinal section, in Fig. 24.

*a* represents the main chamber, the bottom *b* of which is composed of iron bars perforated with small holes of about  $\frac{1}{4}$  inch in diameter and about 1 inch apart, and preferably made slightly conical, with the larger diameter downward, that is to say, the said holes are of such a size as to prevent

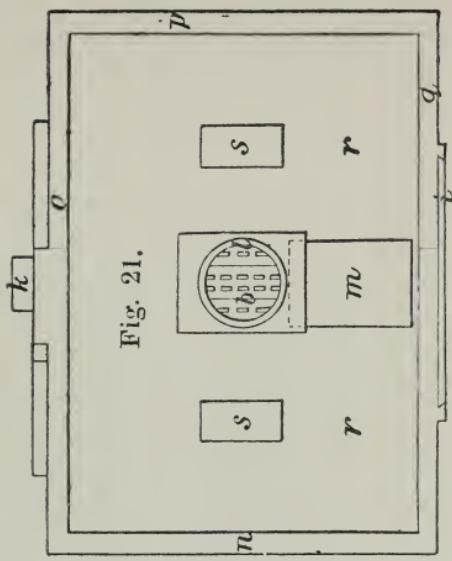


Fig. 21.

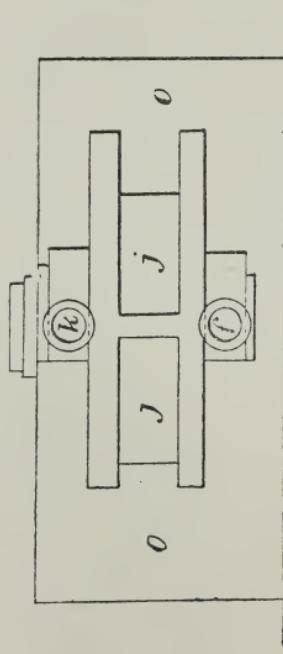


Fig. 23.

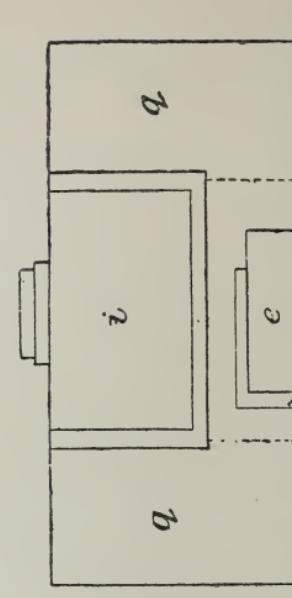


Fig. 22.

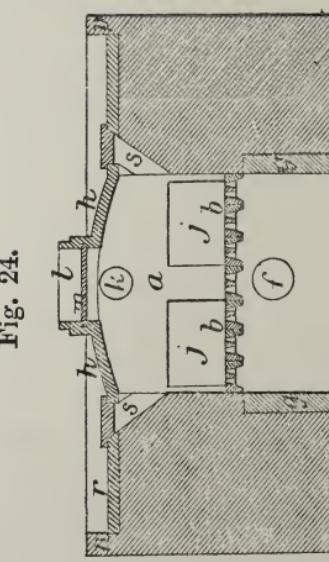


Fig. 24.

the escape of the crushed ore and coal. These perforated bars are suitably sustained at the ends on the front and back walls of the furnace. The ash pit below the perforated bottom is of equal area therewith, and is provided with a door *e* in front, and with a hole *f* at the back for the reception of a pipe from suitable blowing apparatus.

The walls *g*, and arch on the top should be built of some refractory substance, such as fire-brick.

The front of the furnace is entirely open, and is provided with sliding doors *i*, by which it can be closed when working, and opened to remove the residuum.

At the back of the furnace there are two slides *j*, to permit access to the main chamber, for stirring the charge and for inspection.

At the back, near the arch, there is a hole *k*, governed by a sliding damper leading to a chimney, for carrying off smoke and impure gases at the commencement of the operation upon a new charge.

In the centre of the roof there is an aperture *l*, governed by a damper or sliding door *m*, the said aperture leading to a suitable apparatus for the collection of the oxidised vapours of lead.

The exterior walls *n o p q* may be built up to form two feeding troughs *r*, one on each side of the arch or roof, and each provided with an aperture or passage *s*, communicating with the inside or main chamber, and each aperture or passage is provided with a cover to be put on after the furnace has been charged.

In working with this furnace, crushed ore (native sulphuret of lead) and carbon, preferably in the state of pea or dust anthracite coal, are mixed in equal proportions; the mixture is ignited, and the fumes are oxidised by the blast through the mixture, which also promotes the combustion. Dense white vapours or fumes pass off, and are conveyed to a separate chamber, where they are strained by passing through a screen or series of screens of muslin or other tex-

tile fabric. Lime may also be employed in the furnace, in the proportion of 200 lb. of lime to 400 lb. of galena, although the addition of the lime is not necessary in all cases.

Instead of the furnace above described, a muffle furnace may be employed, in which the heat is applied indirectly to the ore, with the precaution of constructing the sole or bottom of this furnace of a material not rapidly acted on by the constituents of the ore ; or a reverberatory furnace may be used in which the heat is directly applied. In both of these two cases reducing carbon may or may not be mixed with the ore.

Sometimes, generated gas is employed in place of coal, to effect the same result.

In a later specification Lewis remarks that when white lead pigment is manufactured from galena or other lead ores, in the raw state, or even in the roasted state, by subjecting them to the joint action of heat and air, either with or without reducing means, according to the quality of the lead ores used, the fumes are discoloured by particles of carbon or sulphuret of lead, or both, when they are caught in bags of textile fabric, and are unfit when in this state for use as a white pigment.

The fumes which are produced by this action of heat and air on galena or other lead ore are cooled and then collected in bags, and Lewis prefers to expose the so-collected products to the joint action of heat and air, to destroy or to burn out all the particles of carbon or sulphuret of lead, or both, by either throwing the said fumes on a bright clean anthracite or coke fire, with a blast from the sides or from below, or by throwing them over such fires or into a cupola furnace, or by throwing or blowing them into a generator gas flame, or through externally heated retorts. He then in either case collects the escaping fumes from the furnace or retort in bags or screening chambers.

The best process to be adopted depends upon the kind of

fuel in the locality where the fumes are refined, and also upon the purity of the lead fumes. If they contain iron, clay, or the like, it is best to throw them into a coal fire; but if they are pure, one process is about as effective as the other, and the degree of purity of the fuel decides the kind of heating apparatus to be used.

There being such great difference in the purity of fuels, and this irregularity not allowing of uniform results, Lewis prefers to use a furnace in which the flame and heat are produced by burning gaseous fuel with air, which is forced into the furnace with the fumes which have been collected in a previous process.

Fig. 25 represents a furnace which may be advantageously employed for the purpose when gas is used as fuel.

*a* represents a blower, into which the fumes are fed from the hopper *b*. The fumes, being thoroughly mixed with air in this blower, are forced into a chamber *c*, and then through a series of tuyeres *d*. At the same time, gas from a generator or producer is admitted by the flue *e*, and is burned by the incoming blast from the tuyeres *d*; the volatile fumes produced in the furnace *f* pass through it and out of the flue *g*, and are collected in bags or screening chambers. By using gas fuel, which is easily and fully burned, and clean to handle, a fine white pigment is produced.

*MacIvor's Processes.*—The name of MacIvor is a familiar one in improvements in manufacturing chemistry, and not the least in connection with the subject of pigments, sometimes in conjunction with other inventors.

In 1889 MacIvor and others introduced some modifications in the process of producing white lead or carbonate of lead, by the treatment of oxide of lead (litharge or massicot) with a solution of acetate of ammonia, whereby the oxide of lead is transformed into hydrate and acetate, which are subsequently converted into carbonate of lead by the injection of carbonic acid. The hydrate and acetate of lead, in presence of free ammonia formed in the reaction, are quickly decomposed by

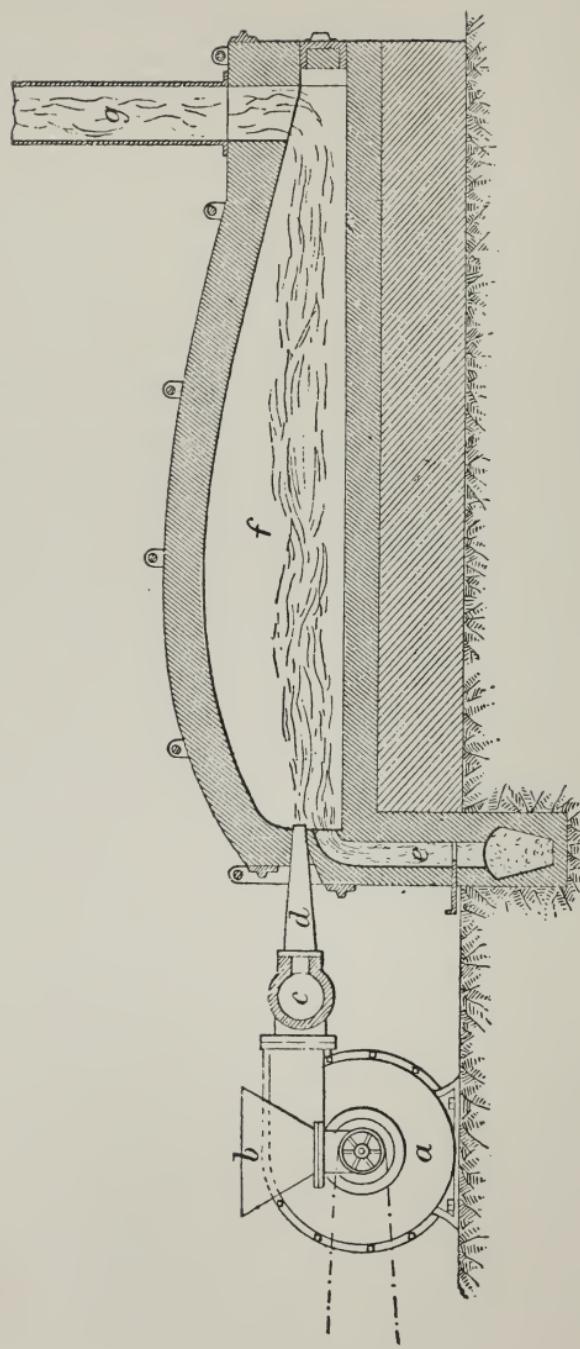


Fig. 25.—LEWIS'S WHITE LEAD PLANT.

the carbonic acid, yielding the final product, namely carbonate of lead, and re-forming the acetate of ammonia.

The rapidity with which the conversion of oxide of lead into hydrate can be effected depends upon the strength of the acetate of ammonia solution employed, that is to say, the weaker the solution the slower will be the conversion. It has been found that, for commercial purposes, the solution of acetate of ammonia may be used with advantage of a strength which need not be more than 25 per cent. nor less than 5 per cent. A strength of 25 per cent. operates in a comparatively short space of time; but a strength as low as  $\frac{1}{2}$  per cent. will effect the hydration if there be a sufficient quantity of the weak solution, the lead oxide being in a fine state of division, and time of no object. This  $\frac{1}{2}$  per cent. strength, however, or any strength below 5 per cent., is not recommended for commercial purposes, having regard to the time required for completing the operation.

The conversion of the oxide of lead into the hydrate and acetate of lead is effected in the cold (heat may be used, but for commercial operation it is not recommended). The conversion is facilitated by employing a mechanical arrangement, similar in many respects to that adopted in a previous specification, but modified by connecting the digesting vat with a cistern or vat containing acetic acid, whereby any free ammonia carried over during the operation may be absorbed. Also by introducing carbonic acid to the mass of hydroxide and acetate of lead formed by the oxide of lead and acetate of ammonia, either by a series of concentric rings perforated with small holes in the bottom of the vat itself, or by passing carbonic acid down a hollow shaft to which are attached stirrers, and through perforated tubes attached to the blades of the stirrers, or by any other means that may ensure the thorough saturation of the hydroxide and acetate of lead so as to form carbonate of lead.

The solution of acetate of ammonia may be recovered from

the white lead, and be repeatedly used for the conversion of further quantities of oxide of lead into hydrate and acetate of lead, which hydrate and acetate are converted into carbonate of lead by the injection of carbonic acid. Theoretically, a given weight of acetate of ammonia in solution, used in conjunction with carbonic acid, should be capable of converting an unlimited quantity of oxide of lead into carbonate of lead ; but during the manufacture of white lead by this process, it may be reckoned that there will be a loss of ammonia acetate varying with the strength of the solution employed, but it should not exceed 10 per cent. on each charge. This loss arises in the washing of the final product, and through the escape of some ammonia during the process.

Fig. 26 is a vertical section of the apparatus employed.

*a* is a vat, which may be made of wood or other material capable of resisting the chemicals employed ; it may conveniently be 6 feet in diameter and 4 feet deep, and it is provided with a closely fitting cover. *b* is a cistern situate at a higher level, and intended to contain a solution of acetate of ammonia. *c* is a pipe by which the solution can be drawn down from the cistern *b* into the vat *a* ; a cock is provided upon this pipe, as the drawing indicates. There is a man-hole *d* in the cover of the vat, and the vat contains an agitator *e*, with a vertical shaft which can be turned by gearing *f* as shown, or the agitator may be driven by any suitable motor. The shaft of the agitator *e* is hollow, and pipes *g*, which stand immediately behind the stirring tines, are connected with the hollow shaft, to deliver the carbonic acid gas into the vat ; or this may be effected by means of coils of pipe laid at the bottom of the vat, and pierced with small holes. The pipes *g* are open at their lower ends. *h* is a cock by which the liquor can be drawn off from the vat into the receiver *i*. A pump *k* is provided upon the cover of the receiver, by which the liquor may be returned into the vat *a*. *l* are outlets by which the white lead is discharged from the

vat into the washing cisterns *m* and *n*. *o* is a man-hole, which may be opened to facilitate the emptying of the vat.

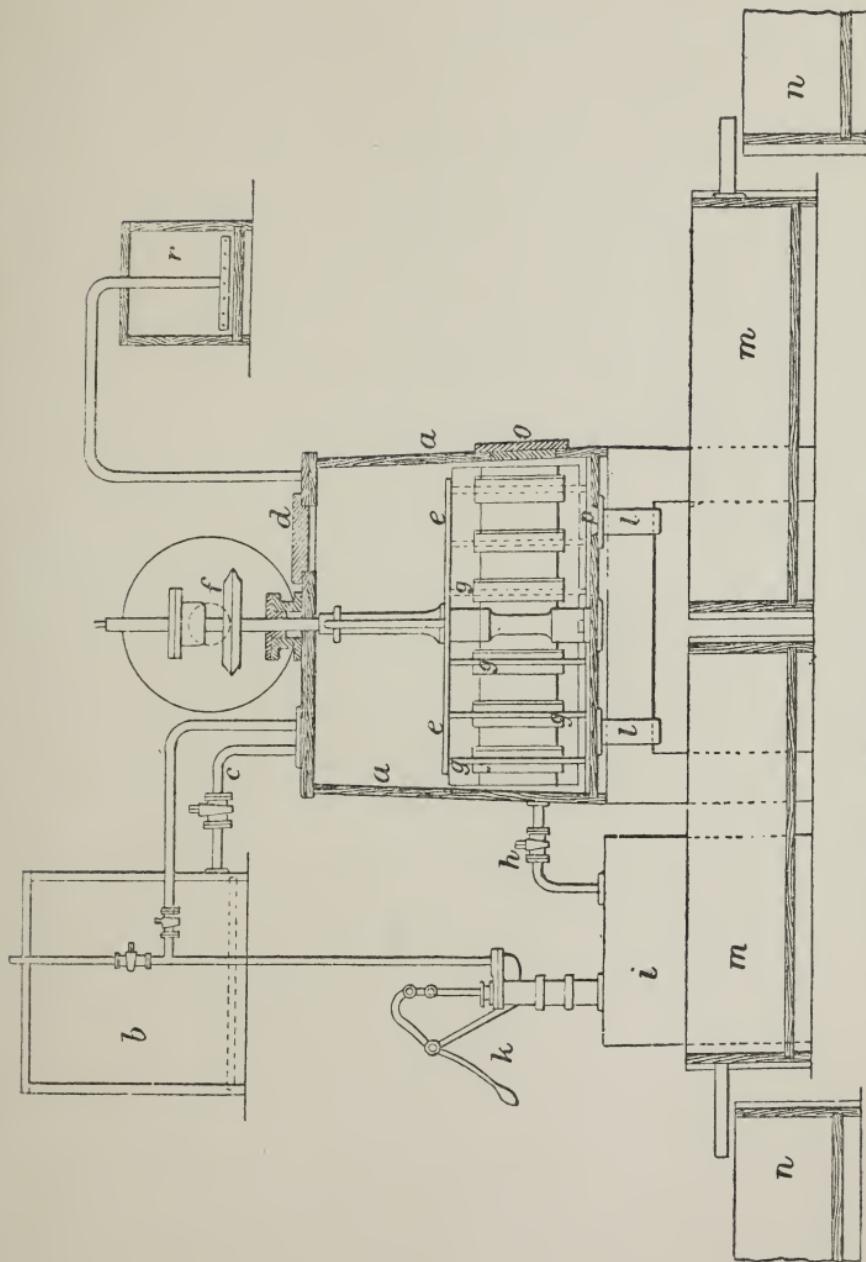


Fig. 26.—MACLIVOR'S WHITE LEAD PLANT.

*p* is a plug which is removed to let the white lead run out of the vat. *r* is an ammonia catch box, charged with acetic acid.

All the metal-work of the apparatus with which the acetate solution comes into contact should be of such a character as to resist corrosion, or should be coated with a material capable of withstanding attack by the chemicals employed in or formed during the process.

The operation is by preference conducted in the following manner, but the details admit of variation. The charge of monoxide of lead for an apparatus of the dimensions indicated may weigh about 1120 lb.

The monoxide should be in fine powder, and may be either moist or dry. Having received this charge, which is introduced by the upper man-hole *d*, the vat *a* is closed, and a solution of acetate of ammonia is let down upon the charge from the cistern *b*, or pumped out of the receiver *i*. The vat *a* should be charged with the solution of acetate of ammonia in the proportion of three parts of said solution to one part of lead monoxide by weight. It is convenient to employ a solution containing 5 per cent. of acetate of ammonia, and the quantities above stated are suited to a solution of this strength; but the strength of the acetate solution may be varied within wide limits, as hereafter explained.

The charge of monoxide of lead and acetate of ammonia in the vat should be kept constantly stirred by the agitator until it becomes whitish in colour, when it will be found that the monoxide of lead has become converted into hydrate and acetate. The workman will know that this change is complete when the reddish or yellowish appearance of the monoxide of lead disappears, and the mass in the vat becomes whitish in colour.

The hollow axis of the agitator is connected with a pipe, by which carbonic acid gas is supplied to it under pressure sufficient to cause the gas to pass through the contents of the

vat. This gas escapes at the lower ends of the pipes *g*, and ascends through the liquid in which the hydrate and acetate of lead are held suspended. A free flow of this gas should be maintained, and some excess allowed to pass away by a pipe on the cover into the ammonia catch box *r*. The pipe dips down into the acetic acid which this box contains, and any ammonia passing off with the carbonic acid gas is caught by the acid, and forms acetate of ammonia. When the hydrate and acetate of lead are completely converted into basic carbonate (and this the workman will know by its changed appearance), the motion of the agitator is caused to cease, and the white lead is allowed to settle.

There is a gauge glass on the side of the vat *a*, and in this glass the changes of appearance can be recognised by which the workman regulates the process.

When the white lead is deposited, the liquor is drawn off into the receiver *i* by opening the cock *h*. The plug *p* is then displaced, and the white lead is allowed to descend into the washing cistern *m*. Below the cock *h* is another cock or cocks, in order that any further quantity of liquor may be drawn off into the cistern *i* if required. The taper plug *p* is then raised, by being pushed up from underneath the vat *a*, through pipe *l*.

The white lead requires to be well washed with clean cold water.

When a fresh charge of monoxide of lead has been placed in the vat *a*, the liquor is pumped up on to it from the receiver *i*, and then a further quantity of solution is drawn from the cistern *b*, and also from the ammonia catch box *r*, until the proper quantity has been supplied, which is determined by the gauge.

Quite recently, in conjunction with Mr. Watson Smith, Mr. MacIvor has introduced further improvements in the production of "white lead" or basic carbonate of lead, by the treatment of oxide of lead (litharge or "massicot") with a heated solution of acetate of ammonium, in a closed vessel

(called the digestor), with agitation and under pressure, so that the oxide of lead is transformed with exceeding rapidity into basic acetate of lead, chiefly consisting of the tri-basic acetate, ammonia being set free; and the subsequent treatment of the basic acetate thus obtained, after filtering or otherwise removing insoluble impurities, and after cooling with carbonic acid gas in a separate vessel (called the carbonator).

The acetate of ammonium is by preference first charged into the digestor, and then the oxide of lead (litharge or massicot) in fine powder, and in the equivalent proportions calculated to be at least somewhat slightly in excess of the quantity necessary to form with the acetic acid of the acetate of ammonium the tribasic acetate of lead  $Pb(C_2H_3O_2)_2 + 2 PbO$  or  $Pb_3O_2(C_2H_3O_2)_2$ , is added (this being in allowance for the certain amount of insoluble and unconvertible matters in the litharge), the acetate of ammonium liquor of a strength preferably not below 5 per cent., though it may be stronger, being first, before the addition of the oxide of lead, set in vigorous agitation and circulation by the pump, and heat having been applied by means of a steam heater as shown in the drawing and as will be explained later on.

The digestor is closed, and the temperature rises. As the temperature rises, and approaches  $212^{\circ}$  F., and as the pressure, due more especially to the tension of vapour of ammonia set free during the reaction with the litharge, increases, so is the rapidity of the conversion of the oxide into basic acetate increased, and more and more of this basic acetate becomes dissolved, whilst at or about  $212^{\circ}$  F. it is entirely in a state of solution. The degree of heat, or the prolongation of the heat, depend of course upon the state of dilution of the acetate of ammonium used. Something more specific will be said later on regarding this question of degree of heat.

The clear liquor, together with extraneous coloured particles, red lead, dirt and undissolved matters, is pumped out through a suitable filter to one of the carbonators, being

carried en route through a cooling-pipe system, and being let cool further if necessary in the carbonator itself. After cooling thoroughly, the cold basic acetate, which may now have crystallised or separated out more or less, according to the strength of the solution, is treated with carbonic acid gas, whereby the basic acetate, in the presence of the ammonia set free, is converted into basic carbonate of lead of exceptionally white colour, and with high basicity and covering power, proper care being taken as specially indicated later on. There are several reasons why greater whiteness of the product is secured, the principal one being that filtration from solid and insoluble coloured impurities has taken place previous to the carbonating process.

The advantages of the employment of heat and pressure for the formation of the basic acetate of lead from oxide of lead, and the advantage of thus carrying out the conversion of oxide into basic acetate of lead separately from the conversion of that basic acetate of lead into basic carbonate or white lead, are—

Firstly—That separation by filtration from impurities and so forth left by the oxide of lead used, and insoluble in the acetate of ammonium, is made possible, and thereby a pigment of exceeding whiteness and purity can be obtained, besides high basicity, with corresponding body and covering power.

Secondly—That the rapidity of the conversion of oxide of lead into basic acetate of lead is immensely increased—it becomes in fact almost instantaneous, much time being saved.

Thirdly—That the conversion is effected quickly and in a perfectly closed vessel; no chance of the escape of ammonia occurs, and, in the carbonating stage of the process, the free ammonia present in the liquid assists in securing the formation of basic carbonate of lead, and the maintenance of this basicity throughout the conversion.

This free ammonia is converted by the carbonic acid into

the less volatile but still alkaline carbonate, and, later on, this ammonium carbonate reacts upon the basic acetate of lead, converting it into basic carbonate of lead, acetate of ammonium, still less volatile, being simultaneously produced, ready for use over again.

It must be understood then, that as the carbonic acid passes into and through the ammoniacal mixture in the carbonator, it continually precipitates or forms basic carbonate of lead, in presence of more or less of the volatile alkali, which however continually diminishes in quantity as the conversion proceeds.

Were no ammonia present, but only tribasic acetate of lead, as in the case of the earlier methods of precipitating white lead, unless a very slow current of carbonic acid gas were passed through, some of the first formed basic carbonate of lead would be in danger of being over-carbonated and losing its basicity, being converted into mono-carbonate of lead. This danger is much lessened, and consequently a much greater possibility of rapidity of carbonating is conferred, in the case of the process as above described, and by virtue of the ammonia which is present.

Nevertheless the carbonic acid gas must not be passed, even into the ammoniacal liquid containing the tribasic acetate of lead, with such rapidity that distinct alkalinity to the usual tests ceases to be maintained, and the process must be terminated whilst the liquid is still alkaline. If a little lead salt on the one hand, and a little ammonia on the other, be left in the mother liquors ultimately obtained on filtering from the white lead, they will be returned and circulated.

Fig. 27 shows an elevation (partly in section) of the apparatus employed.

*a* is an iron vessel made of boiler plate, and lined internally with lead. It may be here added that all the apparatus is thus lined, or is constructed of material invulnerable to the action of lead salts, ammonia, or acetate of ammonia.

The vessel *a*, which is termed the digestor, should be

furnished with a thermometer, pressure gauge, safety valve, charging hole *b*, and suitably arranged sampling pipe with cock.

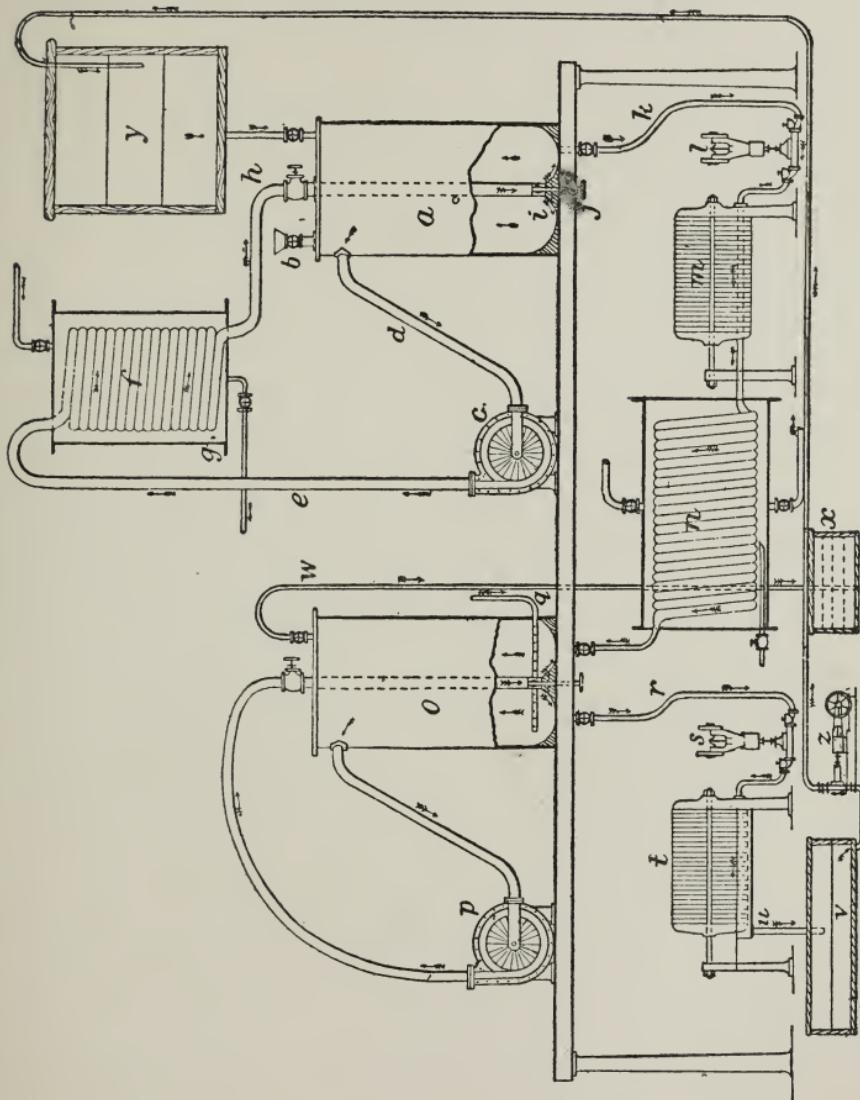


Fig. 27.—MacIvor's WHITE LEAD PLANT.

Agitation of the contents of the vessel is effected by means of the circulating pump *c*, which, drawing off supernatant liquor along with air and ammonia vapour from the upper

part of the digestor *a*, by the pipe *d*, forces it through the pipe *e* to the heater *f*, consisting of a coil suitably heated by steam in a steam vessel *g*, or by similar means, and then is forced through a pipe *h*, leading to the bottom of the digestor *a*, where it terminates in a cone-spreader *i*, provided with a regulating valve *j*. By means of this spreader, the liquid is forced through the heavy and dense mixture containing the oxide of lead, which it vigorously agitates and keeps more or less in circulation as indicated.

The charges of litharge and acetate of ammonium will vary according to the strength of the latter. For a 5 per cent. strength of acetate of ammonium solution, however, it will be best to calculate the proportions as follows, viz. about 1200 gallons of 5 per cent. acetate of ammonium liquor for 1 ton of litharge, which should be finely ground.

The temperature of the liquor may vary between 140° F. and 212° F.; but within these limits, the lowest temperature consistent with the sufficiently rapid conversion and solution of the litharge is preferable. The reason of this is simply that the less the heat employed, the less is the tension of the ammonia, and the chances of the loss of ammonia are thus minimised; in addition to this, less delay is involved and less refrigeration or cooling is needed before carbonating.

The object of the violent agitation of the litharge amongst the heated acetate of ammonium in the digestor *a*, is that caking of the former may be prevented, and a most rapid conversion of the oxide of lead into basic acetate of lead, with minimum expenditure of heat, be secured.

The effect of the heat in the closed space is greatly aided by that of the pressure due to the tension of the ammonia and aqueous vapour at the increasing temperatures.

When the litharge is converted into tribasic acetate of lead, and brought into solution, the liquor and sludge of insoluble matters is preferably pumped through pipe *k*, by means of the filter-press pump *l*, and forced through the filter-press *m*, which removes and retains the insoluble matter, allowing the

clear liquor to pass to the cooler *n*, and through this to the carbonator *o*, similar in construction to the digestor *a*.

Here the cooled liquid is circulated by means of pump *p* (in a similar manner to that adopted in the digestor process already described), carbonic acid being simultaneously pumped in through the pipe *q*, which is perforated as shown, or introduced in any other way.

When carbonated to the desired extent, the white magma, consisting of basic carbonate of lead and mother liquor, is drawn through the pipe *r*, by the pump *s*, into the filter press *t*.

The clear liquid flows through *u*, into the covered mother liquor tank *v*, whilst the press-cakes of white lead, after sufficient washing with water, are removed and dried in a suitable manner.

The washings are run off to a weak liquor tank (not shown) for concentration for use over again. Any inert gases accompanying the carbonic acid, or the latter alone in excess, pass from the carbonator through pipe *w*, into the catch-box or other condensing and absorbing apparatus *x*, containing either dilute acetic acid or cold water, in order to retain any ammonia carried over, and furnished with perforated trays or baffle-plates.

This catch-box is, if necessary, also connected with a further condenser, so as to remove all ammonia from the displaced air, or inert gases (if impure carbonic acid has been used) of the carbonator. It is a lead lined vessel preferably. The ammonia carried from each charge thus is tested by measuring the volume of the solution from the catch-box or other condensing and absorbing apparatus, and estimating the ammonia present in the solution. This amount of ammonia in a sufficiently concentrated form is then added to the charge in the carbonator, when cold, so as to produce a completely neutral solution. The ammonia in the catch-box is either added to the ammonia stock in the ammonia department, used for dilution of strong ammonia in making fresh acetate, or

strengthened up to further absorption in the catch-box or condenser, until strong enough to add to a freshly run and cooled charge in the carbonator, to replace any ammonia driven off by heat.

The sludge in the filter-press *m* is washed with water to remove acetate liquors and ammonia, the weak liquors being run to a separate closed vessel similar to the carbonator *o*, but smaller, and not shown in the drawing.

Here white lead is precipitated by carbonic acid, and the product is passed into the filter-press *t*, the weak liquors associated with it serving to give a preliminary washing to a freshly received charge of white lead already in the press. The weak filtrate liquors thus obtained are preferably sent to the weak liquor tank already mentioned, for subsequent concentration, instead of to the stronger liquor tank *v*.

The sludge-cakes from the filter-press *m*, connected with the digestor, are suitably treated for the recovery of lead therefrom.

The mother liquors contained in tank *v* from the white lead filter-press *t*, are directly returned to the ammonium acetate tank *y*, by the pump *z*, for use over again.

The carbonators may be operated singly as described, or two or three may be connected together so as to be worked in rotation, the partially absorbed carbonic acid from one carbonator being completely, or more or less completely, absorbed in the one, or two, with which it is connected. The last of such series of carbonators would of course be connected with the catch-box arrangement previously described, or other condensing and absorbing apparatus.

*Characters.*—The advantages and disadvantages in the employment of white lead have been described pretty fully by Prof. Barff in one of the Cantor series of lectures which form such an important feature in the publications of the Society of Arts.

Probably the fact that white lead possesses the body it has is the reason why it has been so largely used, and why so

many paintings which have been painted with it have come to a most untimely end. Prof. Barff says he knows of no pigment so liable to change of colour as white lead. In saying this he expects that there are many who will not agree with him. They know that white lead works well and easily, and they like it because it covers down well; but then he points out some of the great defects under which it labours.

If you take some oil, and if to that you add lime-water, the oil will mix with the lime-water, and form a kind of emulsion. Again, if you boil oil or fat with soda, a kind of soap is formed, and the process of manufacturing soap is termed the process of saponification. Now if, instead of boiling fat with soda or alkali, we boil it with plumbic oxide or oxide of lead, we shall form a soap, and that soap goes by the name, amongst medical men, of *emplastrum plumbi*, or lead plaster. This is a substance made by the saponification of oil with the oxide of lead. Because this oxide and carbonate of lead have the power of saponifying oils, you get in white lead that peculiarly smooth easy working which you do not get with any other white pigment; and it is on this account, for one reason, that it is liked by artists and painters. Taking a piece of paper coated with some of this lead plaster, if you throw a light upon it, you will see that the substance is semi-transparent. This is a peculiarity of lead that it will saponify and form this sort of transparent substance.

The famous landscape painter, Mr. Wilson, made an addition to a room in his house. The old part of the room had been painted a dark colour; the new part, of course, when it left the workman's hands, was perfectly white, and therefore the painters painted down the dark colour with white lead, until the whole room displayed one uniform tint. After a while, however, it was found that the part which was originally painted dark became dark again; the dark paint, in fact, showed through the white lead. Sometimes, possibly, when an artist wishes to put in figures upon a dark

background that he has painted, he uses white lead, and the figures will stand out well and brilliantly at first, but after a time the dark colour upon which they are painted strikes through the lead, and the figures of course recede. Now, this striking through is owing to a slight process of saponification, no doubt owing to an interchange between the carbonic acid of the lead carbonate and the stearic and oleic acids of the oil with which the lead is mixed; so that, in time, the white lead, which has a body which makes it so great a favourite with artists, loses that body, and becomes a transparent or semi-transparent substance, something like lead plaster. Here is a reason why white lead should not be used unless the ground has previously been brought to a light colour.

There is another objection to the use of white lead, and really a very valid one it is. Persons go on year after year laying out sums of money for having their houses painted with white lead, when other pigments which will keep their colour might well be employed. A house painted with white lead after some time darkens in tint considerably; the colour is changed by some influence that is acting upon it through the air, and that influence is sulphuretted hydrogen gas. If you paint with white lead doors placed near a drain from which this gas escapes, those doors will become browned and blackened. White lead is very often, particularly that procured at ordinary shops, adulterated with a substance called sulphate of baryta, or, commonly, barytes. This is much more transparent when ground with oil than white lead itself, and it will materially impair that property for which white lead is valued, viz. that of covering down well and solidly. White lead adulterated with barytes has, generally speaking, a bluish sort of look; it is semi-transparent. It has not that opacity that pure white lead has. If you take a small piece of white lead and put it into a test-tube, and add to it a little nitric acid, or aquafortis, and some water, if the lead is pure the whole of it will dissolve in the

liquid, and you will have a pure solution. If it does not dissolve there is a white precipitate, which will fall down to the bottom of the tube, and that precipitate is sulphate of baryta. Sulphate of baryta is insoluble in aquafortis, but carbonate of lead, and most lead salts, are soluble in it.

There is another excellent test for the purity of white lead, which is this. If you take a small portion, and grind it up with a little carbonate of soda into a small pellet about the size of a pea, and then put it upon a piece of charcoal and hold it in the middle flame of a blow-pipe for some short time, the sulphate of baryta becomes decomposed, and you get sulphide of sodium formed. If this sulphide of sodium be acted upon by an acid liquid, sulphuretted hydrogen is given off, which could not be formed from carbonate of lead, for in it there is no sulphur at all; and inasmuch as sulphate of baryta is the impurity for which we have to look, the presence of sulphide after this treatment indicates that it was with the white lead which was examined.

LIME WHITE.—A name sometimes given to the white pigment prepared from sulphate of barium. See baryta white, p. 170.

LITHOPHONE.—This is a fancy title for one of the several varieties of white pigment having the metal zinc as a basis, and described under zinc whites on p. 247.

MAGNESITE.—The mineral known by this name is a natural carbonate of magnesia, just as limestone is a natural carbonate of lime. Where sufficiently abundant it is quarried, ground, and levigated much in the same manner as barytes, which it greatly resembles in its qualities as a pigment, and for which it constitutes a suitable substitute. It is very white, heavy, and opaque; permanent in ordinary situations; neutral with other pigments, mixes equally well with oil or water, and possesses good covering power.

MINERAL WHITE.—One of the names applied to the pigment prepared from gypsum, see p. 183.

ORR'S ENAMEL WHITE.—A name derived from the maker

of a certain variety of the zinc sulphide pigments, described under zinc whites, p. 254.

PARIS WHITE.—Another name for the best brands of whiting, see below.

PERMANENT WHITE.—This name is often bestowed upon baryta white (see p. 170), on account of its durability as compared with white lead.

SATIN WHITE.—There is a certain amount of confusion in the application of this term, for while it is sometimes referred to baryta white (p. 170), it is also a synonym for fine gypsum (see p. 183).

SPANISH WHITE.—The most carefully prepared samples of whiting (see below), are often known by this name.

STRONTIA WHITE.—Though much less common than the closely similar sulphate of barium, the natural sulphate of strontium is equally suitable for employment as a pigment, and is prepared in exactly the same way as baryta white (see p. 170). The artificial product is also used. Both possess qualities remarkably akin to those of baryta white.

TERRA ALBA.—An old-fashioned name for levigated gypsum (see p. 183).

WHITING.—This material is simply prepared chalk. It should be soluble in hydrochloric acid with effervescence, leaving at the most but a small residue. Sometimes samples of whiting are found which are more or less alkaline or caustic in their properties. This is a serious defect for many purposes. It can be detected by treating the sample with water, and adding to the liquor a little phenolphthalein. If a brilliant red colour is obtained, caustic lime is present, and the sample should be rejected, if to be used for mixing with chromes or Brunswick greens, where a neutral product is required.

Chalk itself is too familiar to need any description beyond saying that it essentially consists of carbonate of lime, with always a small percentage of silica associated with it.

Its preparation consists in hand selection to exclude the

silica which occurs in the more pronounced form of flints, then grinding in several stages, levigation and drying. The levigation is effected by having a series of settling pits into which the ground material flows with water, and deposits according to its degree of fineness. The drying is performed in chambers provided either with pipes carrying steam or heated air, or by fires beneath the floor, and thoroughly ventilated so that the moist air can escape as fast as it is saturated. Finally the dried whiting is again ground very fine. The drying must be done with great care and at a low temperature, so as to ensure avoiding calcination, whereby the carbonate of lime is changed into oxide (quicklime).

Whiting is a permanent and useful pigment mixed with water in distempers, but is not applicable as an oil colour.

ZINC WHITES.—Originally and properly the term zinc white was reserved for the white pigment consisting of zinc oxide; but latterly many kinds of white pigment have been introduced containing a large proportion of sulphide of zinc, sometimes associated with more or less oxide, and sometimes without any oxide, and these are also by many people called zinc whites, to which name they are perhaps as well entitled as the original zinc oxide. It will therefore be convenient to arrange them all under the same general heading of zinc whites.

(1) *Oxide*.—Under the influence of a white heat metallic zinc is volatilised, and if the vapour is thus brought into contact with oxygen, either in the pure state or as air, combustion takes place, and the oxygen unites with the metal to form zinc oxide. On this very simple principle is based the manufacture of zinc oxide white.

The operation is conducted in plant similar to that shown in Fig. 28, which consists essentially of two departments, that in which the zinc is volatilised and that in which the oxidised vapour is deposited for collection.

The volatilising process takes place in a series of oblong fire-clay retorts *a*, varying somewhat in form but always

with a contracted and rising neck. Ordinary dimensions are about 2 feet long and 9 inches in diameter each way, with walls about  $1\frac{1}{2}$  inches thick. These are heated to whiteness and then charged with ingots of metallic zinc.

The retorts are arranged in double rows in reverberatory furnaces *b*, two furnaces being arranged back to back so as to economise heat. The furnaces are fired at the side, and the heat is conveyed around the retorts by means of the flues *c*,

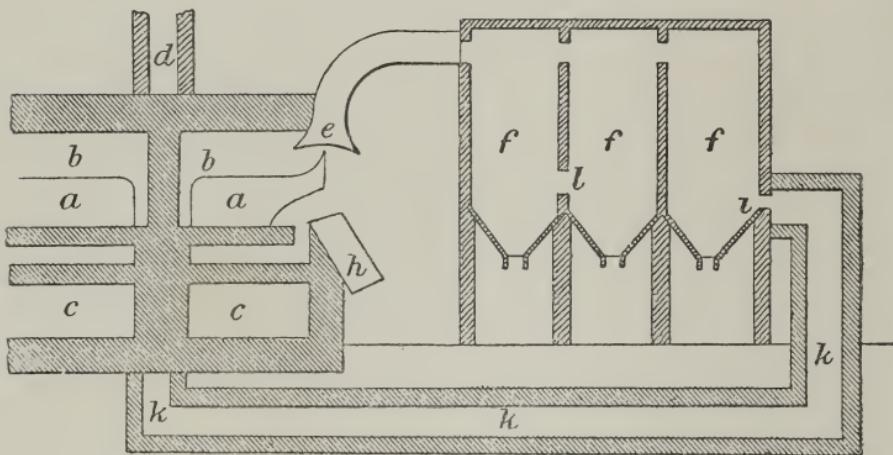


Fig. 28.—APPARATUS FOR MAKING ZINC OXIDE.

the products of combustion of the fuel finally escaping by the chimney stack *d*.

As the vaporised zinc is emitted at the mouths of the retorts *a* in a partially ascending current, it immediately encounters a plentiful supply of air, and thereupon takes fire (undergoes combustion or oxidation). In this condition it enters the lower and funnel-shaped end of the sheet-iron flue *e*, by which it is conveyed into the series of settling compartments *f*.

While the bulk of the zinc oxide thus formed passes into the settling chambers, a portion of it is too heavy to do so; its specific gravity is such that the force of the draught is

not sufficient to carry it up. This portion falls at once into a receptacle placed beneath the mouth of the flue *e*.

In order to obtain the necessary draught, the conduits *h* are open to the outside atmosphere, and introduce a supply of air just below the mouths of the retorts *a*, so that it impinges against the current of escaping zinc vapour. After passing through the settling chambers *f*, the superfluous air finds an outlet at *i* into a sufficiently capacious flue *k*, which communicates with the chimney stack *d*. Thus the draught created by the fuel consumed in the reverberatory furnaces is made to assist the current through the settling chambers.

These settling chambers *f*, are constructed of wood, and are usually about three in number, intercommunicating of course. The zinc oxide enters the first compartment through an aperture in the top of the side to which the discharge end of the iron flue *e* is attached. After traversing the first chamber, the stream of air and such oxide as has not yet settled passes into the second chamber through the orifice *l*, near the bottom of the partition dividing the two chambers. To reach the next compartment, the stream has to ascend again, the aperture being at the top of the partition, and this alternation is carried on to the end of the series, thus checking the through draught and facilitating the settlement of the zinc oxide. The floors of all the chambers are made funnel-shaped, with a door at the lowest point, so that the discharge of their contents may be as automatic as possible. The flue *k* contains screens hung at intervals for the purpose of hindering, as far as possible, the escape of minute particles of zinc oxide into the chimney, and thence into the outer air, whereby they would be lost.

A description of the process as conducted in Belgium, says that ingot zinc is placed in a series of retorts within one furnace, and the oxide is formed in an exhaust chimney, and then passes through a long series of passages and condensing chambers, in which are ranged tanks of sheet iron or cloth

to collect deposits. At a certain hour of the day it is collected into casks, and after being tested as to quality it is ready for delivery. According to the purity of the metal various qualities are produced. The best is called "blanc de neige," or snow white, and is of a very superior quality; No. 1 white is the most used, the ores for this quality being selected and purified by remelting; No. 2 white is the common variety. In the process of manufacture there is more or less waste material, imperfectly oxidised, deposited in the retorts and passages. This residuum is carefully ground, washed and dried, and is employed in painting in the place of lead.

In the American method of making zinc white they use the ore direct. This is cheaper than the Liège method, but its product is of inferior quality to that produced by sublimation. There are but two works in Belgium for making zinc white, the Vieille Montagne Company (at the Valentine Cocq works), which produce yearly 3000 tons by sublimation; the other is at Ougree, near Liège, where the American method is employed, but at present it is idle.

There are many other modifications in detail in different works. One may be noticed here as it is claimed for it that the pigment is gifted with greater covering power or body, the limited degree of which is the only drawback to zinc oxide whites. The plan consists in this, that the oxide is allowed to collect in the condensing chambers till it is of such a depth that a man entering stands waist deep in the pigment. The latter is gathered in pieces of sacking, which are drawn together and squeezed up tightly, so that the oxide, when newly prepared, is pressed into hard dense masses.

(2) *Sulphide*.—Prof. Phipson, in a paper read before the International Health Congress, at Paris, remarked that for several years efforts had been made to discover some white substance to replace white lead for painting buildings, ships, &c. He himself had devoted several months to this important subject, but without success. There has been found,

it is true, in oxide of zinc a substance less poisonous than lead, and serving very well as a white pigment in oil painting; but its production is very expensive, and its mechanical properties as a colour in oil are not pronounced enough to allow it to compete in commerce with white lead. Such is not the case, however, with an invention of Mr. Thomas Griffiths, of Liverpool, who has succeeded in obtaining a very interesting product. This new preparation, which is being manufactured at the present time on a pretty extensive scale, has for its base sulphide of zinc (or an oxy-sulphide of that metal), the properties of which as an oil colour are of the most remarkable character. It is prepared by precipitating one of the salts of zinc by a soluble sulphide, and washing and drying the precipitate. The latter is then calcined at a red heat, with some precautionary measures, then taken from the furnace, and, while still warm, thrown into cold water. It is afterwards levigated and dried. The result is a white pigment, very fine, and of great beauty. Regarded from a hygienic point of view, Griffiths' new white is infinitely superior to white lead, as it also is in its practical bearing; it possesses no injurious qualities; its manufacture and use do not affect the health of workmen; its durability in climates of the most diverse kinds is, so to speak, illimitable; it is altered neither by gaseous emanations nor by dampness; and its price is comparatively low. The most remarkable thing about this new white is that it covers as well as white lead, while it withstands the effects of all kinds of weather, so that its use is not only deprived of all danger to health, but it is much more economical than white lead. Prof. Phipson stated to the Congress that he regarded this new chemical preparation as being among the most ingenious and useful products that have been discovered in our time.

A later method, introduced by Griffiths and Cawley, consists in making an artificial sulphide of zinc by bringing the vapours of zinc and sulphur into intimate contact.

In carrying out this process, sulphur is melted in a jacket pan heated preferably by high pressure steam. The melting vessel is connected with a cast-iron still by means of a jacketed pipe, and the connection is regulated by means of a valve in the bottom of the melting pan. The latter should be at such a height above the still that the pressure due to the column of sulphur in the conduit pipe may be greater than the tension of the sulphur vapour in the still, so that when the valve is opened, the sulphur in the melting pans may descend into the still. The still is kept during the process at a temperature of incipient redness, so that when the sulphur reaches it, the sulphur is immediately vaporised and the resulting current of vapour passes to the chamber described below.

Metallic zinc is melted in a retort or crucible, heated preferably by means of a furnace on the Siemens or a similar principle, and raised to such a temperature that it begins to volatilise freely. When this takes place, the resulting zinc vapour is met by a current of sulphur vapour obtained as above described, and in excess of that required to form with the zinc sulphide of zinc. The reaction takes place according to the chemical equation  $Zn + S = ZnS$ .

The sulphide of zinc is in the form of white extremely light powder, which is carried along by the current of sulphur into the collecting chamber, such as is used for the manufacture of oxide of zinc. This allows of the separation of the different constituents of the products into different qualities; those parts that are carried the farthest are the whitest and best generally. Those portions nearest to the part of the apparatus where combination takes place may sometimes contain metallic zinc, if the sulphur supply has not been carefully attended to, but this may be separated from the sulphide by levigation.

The collecting apparatus should be kept at a temperature slightly superior to that of the boiling point of sulphur, in order that sulphur, which is necessarily in excess, may not

be deposited with the sulphide of zinc, but may pass on in the vaporous form to a suitable condenser, where, after condensation, it may be collected and used again.

Before the sulphur vapour reaches the condenser, the last traces of sulphide carried along with it are collected by the interposition of metallic screens or sieves, placed between the sulphur condenser and the apparatus.

In carrying out the process, care must be taken to keep the collecting apparatus as cool as possible consistently with the fulfilment of the conditions above mentioned, viz. that no sulphur be condensed therein. In practice, this object

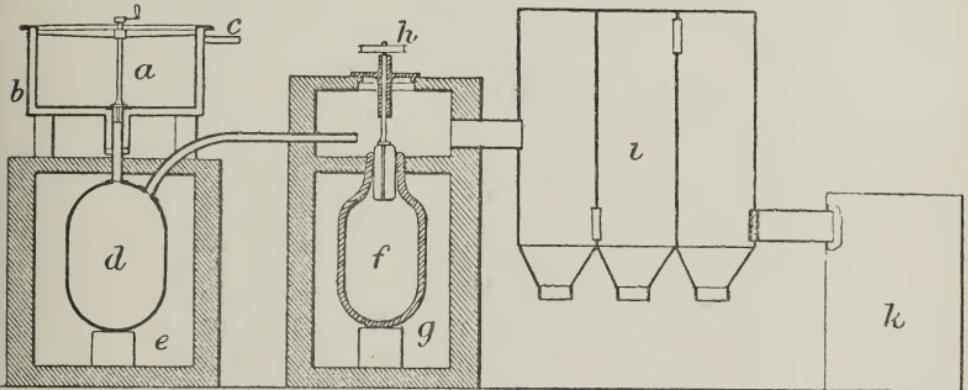


Fig. 29.—APPARATUS FOR MAKING ZINC SULPHIDE.

can be effected with little difficulty. Impurities in the zinc and sulphur are of little consequence provided they are not volatile, and not of such a nature that they would detract from the whiteness of the sulphide of zinc formed.

The accompanying diagram, Fig. 29, is given as an example of a plant that may be employed with good results.

*a* is the sulphur melting pan with its steam jacket *b*, and steam pipe *c*; *d* is a cast-iron still, arranged within a gas furnace *e*; *f* is a crucible for melting and volatilising zinc, the said crucible being contained in a gas furnace *g*; *h* is an automatic apparatus for freeing the mouth of the zinc vessel

from deposited sulphide of zinc; *i* is the collecting apparatus; and *k*, the condensing apparatus.

(3) *Mixtures*.—There are a number of compound pigments commonly known as zinc whites, which only deserve the name in so far as they contain a proportion, greater or smaller, of some zinc salt. At the same time it must be admitted that some of these combinations possess very good qualities, and that the foreign ingredients largely correct the weak points of the zinc compounds.

*Freeman's*.—This pigment, when ground with oil in the customary way, forms a paint equal in body and covering power to the best white lead, while it is superior in colour, permanence, and density, and is free from odour and noxious qualities.

It is produced by grinding together "zinc white" (either oxide or sulphide), lead sulphate and barium sulphate, in certain proportions, in the dry state, in an edge-runner mill. By thus grinding the several pigments together, their particles become intimately incorporated and undergo changes in character. The barium sulphate not only cheapens the product by reason of its low cost, but also imparts a distinct feature in rendering the paint more free working. The proportions generally adopted, calculated by weight, are 5 parts lead sulphate, 2 of zinc white, and 1 of barium sulphate. The duration of the grinding will necessarily vary in accordance with various governing conditions, but it should be continued until the mixture has a density of about 200 lb. per cubic foot.

*Orr's*.—The pigment known as Orr's enamel or Charlton white, is a compound of oxide and sulphide of zinc and sulphate of strontia, or of baryta. It is prepared in two ways.

(a) Barytes is calcined for some hours at white heat with charcoal, and the calcined mass is lixiviated with water to wash out the barium sulphide; to one-half of this solution is added zinc chloride, which produces a precipitate of zinc

sulphide, leaving barium chloride in solution. To this mixture of zinc sulphide and barium chloride is added the remaining half of the barium sulphide and some zinc sulphate, the result of which is a double precipitate of zinc sulphide and barium sulphate. This is water-washed, filter-pressed, dried, calcined at red heat, thrown immediately into cold water, ground very fine, and finally dried.

(b) The second process closely resembles the first, but celestine takes the place of the barytes.

Either form of Orr's enamel is a good useful white pigment, very permanent, mixing well, of excellent covering power, and pure in colour.

*Characters.*—Zinc oxide, being an expensive pigment, is liable to adulteration ; fortunately, all such adulterations are easily detected, and their nature ascertained by a few simple tests. Zinc oxide, if pure, should dissolve entirely without effervescence in nitric acid ; any residue would indicate adulteration with barytes or china clay ; the former may be distinguished by its weight and the yellowish green colour it imparts to the Bunsen flame, the latter is lighter and gives no colour to the Bunsen flame. Boiled with strong sulphuric acid, barytes is not acted on, while china clay is. If, after cooling, the mass be diluted with water, and ammonia be added to the liquor, if barytes is present no precipitate will be obtained, while if china clay is present a white precipitate is produced.

If the zinc oxide dissolves with effervescence, white lead or whiting may be present ; the solution should give no precipitate of black sulphide of lead on passing sulphuretted hydrogen through it. On neutralising the solution in nitric acid with sufficient ammonia, and adding ammonia sulphide to precipitate all the zinc (the precipitate should be white, any other colour would show some impurity), filtering off and adding a little oxalate of ammonia, no white precipitate of calcium oxalate should be obtained ; such a precipitate would show presence of whiting or gypsum.

The white pigments having as a base the sulphide of zinc, also contain barytes, oxide of zinc, sulphate of strontium, &c. They can be distinguished by evolving sulphuretted hydrogen gas, recognisable by its odour, on treatment with an acid. They are not entirely soluble in acids, the residue being mostly barytes, but may also be sulphate of strontium ; it is immaterial whether the two be distinguished or not.

## CHAPTER VIII.

**YELLOWS.**

THE yellow pigments do not form a large or important group, and beyond a few organic colouring matters which have a limited use in artistic painting, they are chiefly confined to the ochres of natural origin and to the chromes, and one or two other kinds artificially prepared from mineral substances.

ARSENIC YELLOW.—Another name for Orpiment (see p. 280).

AUREOLIN YELLOW.—This colour is prepared by precipitating carbonate of cobalt from a solution of a cobalt salt with carbonate of potash; this precipitate is dissolved in acetic acid, and to it is added nitrite of sodium; nitrite of potassium and cobalt are thrown down as a yellow powder. Experiments made on the freshly-precipitated colour prepared in this way, have proved it to be invariably destroyed by caustic potash; but aureolin yellow prepared in another way, put into a flask with some caustic soda, has remained unchanged for several days, and proved to be perfectly stable under this treatment. Samples of the same yellow, exposed to the action of ammonia, soda, and potash for a considerable length of time, have not changed. This is really a most important fact, because aureolin yellow is so beautiful a pigment that one wishes it would stand for ever. It is, in fresco and silicious painting, a great desideratum to have colours that will stand the action of lime and caustic alkalies. Our colours for fresco painting are very limited, and if aureolin will stand the action of caustic alkalies, it may be safely used both for fresco and silicious painting.

CADMIUM YELLOW.—The pigment known as cadmium yellow is important on account of its permanence and brilliancy. It is prepared by passing a stream of sulphuretted hydrogen gas through a slightly acid solution of a salt of cobalt, usually the nitrate or sulphate, whereby the sulphide of cadmium is precipitated as an impalpable powder. It is filtered off, well washed with water, and finally dried at a low temperature.

By this method there is considerable difficulty in producing any precise shade of yellow, which is dependent on the proportion of precipitant used, and can only be controlled after long practical experience. Therefore some modifications have been introduced with the object of securing definite tints. The ordinary colour is a pure chrome yellow. For a lemon-yellow shade, a solution of yellow sulphide of ammonium is added to one of sulphate of cadmium. For an orange tint, the cadmium solution (chloride or sulphate) is made very acid by addition of hydrochloric acid before passing the sulphuretted hydrogen; or the cadmium solution, as for lemon-yellow, is boiled, and receives the ammonium sulphide solution while still boiling. But none of these modifications results in a really durable pigment, on account of the presence of traces of free sulphur or acid.

The best brands of this pigment being somewhat expensive, there is great inducement for adulteration, which usually takes the form of orpiment or of chrome. The former can be detected by the ordinary tests for arsenic, and the latter by the process described on p. 266.

CHROME YELLOWS.—A very important family of yellow pigments are the “chromes,” consisting mainly of chromic acid in combination with lead, iron, or zinc.

Chromates of lead, says Prof. Barff, are produced by precipitating a lead salt with a salt of chromic acid, and the difference in tint is owing to the different quantity of the chromic acid which is present in the salt. The orange chrome is a basic chromate of lead, and basic chromate of

lead contains more of the chromic acid than is present in the lemon chrome. The lightest chrome contains some sulphate of lead precipitated with the chromate. All these colours contain lead, and are therefore liable to the influence of sulphuretted hydrogen. Now, if a chromate of lead is bought hap-hazard anywhere, it may or may not be pure, but generally speaking, unless the chromates are obtained from makers who are careful in the preparation of their colours, they contain many other substances besides chromate of lead. For instance, they contain a quantity of the solution, in a dry state, from which they have been precipitated, and are by no means pure. Obviously, also, there is an inducement to men who sell cheap colours to adulterate them, to bring them down with whiting, and so forth. In that case the chrome loses its body ; if it is brought down with lead sulphate it has more body ; but when chrome yellows are prepared and mixed with good oils, and put on carefully, and those oils have time allowed them to become oxidised, perfectly dry in fact—not dry in the sense in which an artist considers a painting dry, but perfectly hard—then the action of sulphuretted hydrogen in the atmosphere will not be of such great moment as if the colours are impure, or if they are submitted to the influence of that deleterious gas before they have become perfectly hard.

Another objection to the chromes, on the authority of Prof. Barff, is that they are soluble in alkali, and so are many other colours. If a painting is painted with chromes, and if that painting be washed with an alkaline soap, it is quite certain that some of the chromates will be dissolved. Consequently the minute and delicate touches, upon which the artist depended for some of the best effects of his picture, are removed with soap and water. No painting should ever be washed with soap and water at all ; but there are certain colours which will withstand the action of soap, even if it is intensely alkaline, while others will not. Taking a precipitate of lemon chrome, if we act upon this with potash or

soda, it dissolves up the yellow precipitate, and destroys it altogether.

According to Weber, the preparation of chrome yellow presents difficulties in practice, because products differing in shade and structure, although of uniform chemical composition, are obtained according to modifications of the method of manufacture or nature of materials employed. A special difficulty is the turning of colour, whereby a "turned" yellow has a dirty orange-yellow colour, which when mixed with barytes gives a yellowish-brown leather-coloured shade and not a light pure yellow. Other derived colours are similarly affected.

*Lead Chromates.*—The acetate and nitrate of lead are the soluble lead salts generally used. Basic carbonate of lead (white lead) is also much used, the yellows prepared from this material being cheaper, having a large covering capacity, and being particularly adapted for ordinary greens; but these have not the smoothness and lightness so much prized in some of the yellows obtained from soluble lead salts. The oxide, sulphate, and chloride of lead have been proposed for the manufacture of chrome yellow, but their treatment would be very tedious and the products obtained only of medium quality. In the manufacture of chrome yellow from acetate of lead and bichromate of potash, different proportions of these materials are given by different authorities, but some of these are obviously wrong where an excess of bichromate is to be used, for every light chrome yellow is liable to turn by the action of chromic acid or a chromate and thereby become of little value. Proportions should be used, whereby the acetate of lead remains in excess, and the reaction should take place in a solution as cold and dilute as possible. In this way a brilliant yellow tint is obtained.

For the lighter chrome yellows, lead sulphate is precipitated simultaneously with the chromate by adding sulphuric acid or a soluble sulphate to the solution of the bichromate;

these yellows have less tendency to change colour than the pure chromate of lead, if the above precautions are observed. Chrome yellow, precipitated from an excess of lead acetate solution, by means of potassium bichromate, corresponds to the formula  $PbCrO_4$ . When dried it forms light pieces, which show a conchoidal fracture. A still more voluminous product corresponds to the formula  $PbCrO_4$ ,  $PbSO_4$ . The yellow having the composition  $PbCrO_4$ ,  $2PbSO_4$ , is very heavy and shows a smooth fracture. Lightness is often imparted to chrome yellow by the addition of magnesium carbonate.

Nitrate of lead offers no advantages over the acetate, and is generally more expensive to use. Free nitric acid is more objectionable than free acetic acid, because it may act as a solvent on chrome yellow and liberate free chromic acid, which is liable to "turn" the yellow. When using lead nitrate it is preferable to neutralise potassium bichromate with soda, to avoid the presence of free nitric acid. The yellows mostly in demand are the inferior qualities, prepared by mixing pure chrome yellows with white mineral matters, generally barytes, gypsum, and kaolin, usually stirred in with the bichromate solution before adding the lead salt. Barytes injures the colour least, but kaolin has the advantage that it does not increase the weight of the colour so much. Gypsum occupies an intermediate position; it is much more voluminous than barytes, and does not injure the colour so much as kaolin, but it is generally used together with barytes. It is not advisable to use this combination, for the reason that the colour on drying forms very hard pieces, which offer difficulties in grinding. Gypsum, too, from being more easily acted on by reagents than barytes or kaolin, tends to take part in the reaction by decomposing the potassium bichromate before the addition of the lead salt, and this is objectionable. (Weber.)

A writer in the *Chemical Trade Journal* gives the following formula for the production of various yellows:—

## (1) For soluble lead salts :—

	Kilos.
Lead acetate .. .. .. .. .. ..	100
Potassium bichromate .. .. .. .. ..	18
Sulphuric acid (66° B.) .. .. .. .. ..	12

This mixture yields a yellow of the formula  $\text{PbCrO}_4$ ,  $\text{PbSO}_4$ . To obtain good shades, the amount of water employed should not be less than 1000 litres, or double as much with the nitrate. In the latter case, it is better to neutralise the lead nitrate and to replace the acid by the sulphate of an alkali or of magnesium, or preferably of aluminium; for the neutralisation of the bichromate, the best substance is magnesite. The formula thus becomes—Lead acetate and bichromate as before; magnesite, 6 kilos.; aluminium sulphate, 27 kilos.

(2) The Basic Acetate Method.—Litharge, 76 kilos.; acetic acid (30 per cent.), 42; bichromate, 21·5; sulphuric acid, 21·5; water, 2000 to 3000 litres. To obtain a denser chrome, 10 kilos. of soda should be added to the acetate, and 5 of the sulphuric acid replaced by 10 of aluminium sulphate. For the production of an orange chrome, the following formula is given: Litharge, 76 kilos.; acetic acid (30 per cent.), 42; bichromate, 24; Solvay's soda, 15; and caustic soda (100 per cent.), 5. Care must be taken that the temperature does not rise sufficiently high to spoil the shade.

(3) The White Lead Method.—In this case the white lead must be in the finest state of subdivision possible, and suspended in the water: White lead, 100 kilos.; nitric acid (36° B.), 12; bichromate, 13; and aluminium sulphate, 10; or nitric acid (40° B.), 44; bichromate, 24; sulphate, 20, the latter giving the more fiery shade. For the production of an orange: white lead, 100 kilos.; nitric acid (36° B.) 18; bichromate, 28; and caustic soda, 8, the latter being best added to the bichromate before precipitation, and the temperature kept between 150° and 165° F.

(4) The Basic Chloride Method.—The same proportions and temperature are suitable here as in the case of the white lead.

(5) The Sulphate Method.—Lead sulphate, 100 kilos.; bichromate, 24 to 25; Solvay's soda, 8·75 to 16; ammonia (24 per cent.), 1 to 2; and acetic acid (30 per cent.), 5 to 10. The sulphate, in the form of a cream, is gradually added to the other ingredients after solution.

A new and improved process for manufacturing from galena chemically pure chrome yellow having great colouring power, according to the *Paper Trade Journal*, consists in first dissolving pulverised galena with nitric acid to produce liquid nitrate of lead, and then precipitating the chromate of lead by subjecting the nitrate of lead to the action of bichromate of potash, neutral chromate of potash or chromate of potash-soda.

The galena (sulphide of lead) is first pulverised by suitable means, and in case it contains foreign minerals or other impurities, it is washed or otherwise treated in a suitable manner to remove these substances. The pulverised galena is then placed in acid-proof vessels and is dissolved by adding nitric acid diluted with water, the entire mass being well stirred. A slow dissolving takes place at the ordinary temperature; but when the mass is heated artificially, either by heating the vessel, or by using hot water added to the nitric acid, or by the use of steam, more rapid solution is effected. The product obtained is nitrate of lead in a liquid state.

The quantity of nitric acid necessary for dissolving a certain quantity of galena depends on the percentage of lead contained in the ore, and to a certain extent on the amount and nature of impurities present in it, and also on the length of time in which the dissolving takes place. In treating 100 lb. of galena having 80 per cent. of metallic lead, about 90 to 100 lb. of nitric acid of 36° to 38° B. are used, and the nitric acid is diluted with 100 to 200 lb. of

water. This mixture is left for about 24 to 36 hours, and is stirred up occasionally, as above stated.

After the galena is dissolved by the nitric acid, and the sulphide of lead is changed into liquid plumbic nitrate, then the sulphur which floats occasionally on the surface of the solution is removed, and the substance which remains undissolved is washed out and is also removed. The liquid nitrate is then passed through filters of felt, linen, hemp, flannel, &c., or is left standing for about 12 to 18 hours for settling and clearing.

Now in order to produce the chrome yellow from this nitrate of lead, bichromate of potash is dissolved in water, and a sufficient quantity of this solution is poured into the plumbic nitrate solution until all the plumbic nitrate is changed into chromate of lead, called "chrome yellow." Instead of the bichromate of potash, neutral chromate, or chromate of soda may be used, and for the purpose of obtaining lighter tints they may be tempered with sulphuric acid or any other compound of sulphur. The liquid nitrate of lead is placed, preferably, in large open receptacles of wood, clay, earthenware, or other suitable material, and the chromate of potash solution is put into similar vessels, and then placed above the receptacles containing the plumbic nitrate. The chromate of potash can then easily be run into the lower receptacles containing the liquid nitrate of lead, and this mixture is constantly agitated by similar means until all the plumbic nitrate is changed into chromate of lead, which is precipitated on the bottom of the larger receptacles.

The chemical action which takes place by this changing of nitrate of lead into chromate of lead is that the chromic acid of the potash assumes the place of the nitric acid, which parts from the lead and combines with the potassium, so that the lead as chromate of lead is precipitated on the bottom of the receptacle, while the nitric acid of the plumbic nitrate remains with the potassium, which latter has parted with its

chromic acid, and a quantity of water as solution above the chromate of lead.

To change the nitrate of lead recovered out of the 100 lb. of galena above mentioned into chromate of lead, about 56 lb. of bichromate of potash are used. This change usually takes place in from about 10 to 30 minutes, after which the chrome yellow (chromate of lead) is left for a few hours to settle, and then the solution standing on top of the chrome yellow is drawn off by suitable means, or run out of the vessel by opening a cock placed above the level of the chromate of lead.

The latter is then washed by adding pure water, which is poured upon the chrome yellow, and the mixture is stirred up, so that all the remaining liquid nitrate of potash is removed. After this is accomplished, the mass is left to settle, and the water is again drawn off from the precipitate, which then settles on the bottom of the receptacle. This washing is repeated as often as is deemed necessary.

The chrome yellow is next placed in suitable receptacles, and dried in the open air or in specially constructed drying rooms, after which it is packed in boxes, kegs, &c., and is then ready for use. The liquid nitrate of potassium, or saltpetre lye, removed from the receptacles in which the chrome yellow is precipitated, and the first water used for washing the chrome yellow, as above described, are placed in large open flat receptacles or excavations, so as to be exposed to the action of the air and sun; or the liquids may be operated on by a small graduation work, so that a great portion of water evaporates. The residue is then heated in suitable vessels or troughs by a slow heat until a salt crust is formed, which, when cooled off and left to dry, is nitrate of potassium or saltpetre in a pure state.

From 100 lb. of galena having 80 per cent. metallic lead, some 28 to 30 lb. of pure and dry saltpetre are produced by the above described process. The sulphur produced by the dissolving of the galena by nitric acid is melted in a small

stove or furnace in the usual manner, and then refined, so as to produce bars of sulphur called "brimstone." About 10 lb. of such sulphur are produced from 100 lb. of such galena treated in the manner described.

The chrome yellow thus produced is said to be chemically pure, and of great covering power, equal to the best chrome yellow in the market.

The process is very simple, and the crude lead ore is transformed into chrome yellow in from three to four days.

**Characters.**—Pure chromate of lead has an orange-yellow colour, and in whatever manner it be made it always has this tint. Commercially, chromes are made of a great variety of tints, from a pale-lemon chrome to a deep scarlet, through all the intermediate shades of yellows and oranges; in fact, most colour makers produce not less than eight, and some more shades of chromes, whence it is obvious that they cannot be chemically pure, but must be mixed with some other bodies.

In commerce, chromes are distinguished as "pure" and "common": the distinction between them is that the "pure" chromes are made from a lead base, and consist of chromate of lead mixed to a larger or smaller amount with sulphate of lead, the paler shades containing most of the latter; while the "common" chromes are mixed with china clay, barytes, gypsum, or similar bodies.

To distinguish the two kinds of chromes, treat with boiling hydrochloric acid. If pure, the chrome will completely dissolve, the solution usually having a green colour. On cooling, crystals of lead chloride separate out. The liquor will give a white precipitate with barium chloride.

By taking a weighed quantity of chrome, dissolving in hydrochloric acid, adding excess of barium chloride, filtering, thoroughly washing the precipitate with *boiling* water, drying and weighing it, and making the necessary calculations, every one part of the precipitate being equal to

1·3 parts of sulphate of lead, the quantity of the latter in the chrome is obtained.

The "common" chromes, which mostly contain barytes, are not completely dissolved on boiling in hydrochloric acid, the barytes they hold being left as an insoluble residue. By taking a weighed quantity of the chrome, and filtering off, drying and weighing the residue, the amount of barytes present can be ascertained; the solution can be tested for sulphate of lead, which they sometimes contain, as described above.

Chrome yellows and oranges should be assayed for colour and tint, care being taken to compare them with a thoroughly reliable standard sample. Their colouring power and body should also be assayed. Another property which should be tested is the colour that they yield on mixing with Prussian blue. A great deal of chrome is used for making greens by mixing with Prussian blue, and as there is a very considerable difference between them in the shade of green they give, it is rather important to test this property, which can readily be done by mixing 100 grains of the chrome with 10 grains of Prussian blue, grinding them together in a mortar, and observing the shade of the green which is produced thereby; if the green is not bright and pure, the chrome is not fit to be made into greens, and should be rejected for that purpose.

*Iron Chromate.*—If a solution of chloride of iron acidulated with hydrochloric acid be added to neutral chromate of lead, a light orange powder is precipitated, which is chromate of iron. Dried at 104° F., it is found to consist of 65 to 65·11 chromic acid, and 34·58 to 34·78 oxide of iron. Chromate of iron is insoluble in water, dissolves easily in hydrochloric, nitric, and sulphuric acids, and decomposes when mixed with soda lye. Under strong heat, it melts into a brownish mass. It may be used in painting in oils, as a substitute for chromate of lead. Although inferior to the latter in brilliancy, it has certain advantages over it—it does not blacken

with exposure to sulphuretted hydrogen, is not injurious to the user, and withal is cheaper.

*Zinc Chromates.*—The before-quoted writer in the *Chemical Trade Journal*, speaking of zinc chromates, says that although it is possible to prepare lead chromates having shades varying imperceptibly from the palest lemon to a deep granite red, in the case of the zinc compounds scarcely any variation from the normal is possible, this being, however, different from anything obtainable with lead. Zinc yellows fall considerably below the ordinary chromes in their colouring power, but they are faster in light and are less poisonous. More than 80 per cent. of the amount annually made in Germany is used for the production of zinc green by mixing with Prussian blues, of which substance Holland, Switzerland, and Hungary are the greatest consumers. The zinc yellows met with in commerce vary in their constitution considerably, being usually acid chromates of zinc and potassium, basic zinc chromates being rare. Ordinary salts of zinc invariably contain small amounts of iron, which must be removed before they are used in the manufacture of colours. The simplest method is to heat them with the quantity of permanganate theoretically necessary to convert all the iron present into the ferric state, adding zinc hydrate, which need not be free from iron ; after thorough stirring, the whole is allowed to settle, and filtered, when the liquid will be found to contain not a trace of iron.

On the addition of chromate to such solutions, a yellow precipitate ( $ZnCrO_4$ ) falls, but owing to its great solubility in the liquid this process is valueless. By using an excess of bichromate, the zinc chromate combines with some of the alkaline salt, forming the compound  $(ZnCrO_4)_3 \cdot K_2Cr_2O_7$ , which may be washed without loss ; but on drying yields an extremely hard, sandy powder, possessing, in spite of its fine colour, no value as a pigment. By neutralising the two solutions before precipitating, a much higher yield of chromate is obtained, but still so much chromic acid is lost as to make the process too expensive to pay. Formerly an ad-

dition of calcium chloride was made to the neutral solutions, so as to precipitate as calcium chromate some of the acid which remained mixed with the zinc salt. The best results, both in regard to yield and colour, are obtained by adding to the zinc salt sufficient alkali to decompose one-quarter of it, so that the chrome may have the formula  $(\text{ZnCrO}_4)_3 \cdot \text{ZnO}$ . To the bichromate, enough alkali should also be added to convert it into the normal salt. It is to be remarked that the nature of the metal combined with the chromic acid has the greatest influence on the shade of the zinc yellow, so much so that in manufacturing "acid" zinc yellow, the use of sodium bichromate is inadmissible. A basic zinc yellow prepared from the sodium salt has a redder and more cloudy shade than one made from the potassium compound, but the difference is hardly noticeable when sodium-potassium chromate is employed.

Modern zinc yellows are invariably prepared from acid solutions, and consist of a double salt of zinc chromate and potassium bichromate, mixed with a varying amount of unchanged zinc oxide, which must not be regarded as an adulteration of the pigment, for its presence gives the substance "body." As previously stated, sodium bichromate is inadmissible, as it does not form similar double salts.

The raw material is usually zinc oxide, which is met with in a state of great purity; by the addition of sulphuric acid, this is converted into basic zinc sulphate; potassium bichromate solution is added, and the whole is stirred vigorously for an hour. At the end of this time, the zinc chromate, which was previously in a state of partial solution, begins to separate out in the form of a brilliant yellow scum on the surface of the liquid, consisting of  $(\text{ZnCrO}_4)_3 \cdot \text{K}_2\text{Cr}_2\text{O}_7$ , while the solution rapidly becomes almost colourless. Suitable proportions are:—Zinc oxide, 100 parts; sulphuric acid (66° B.) 60; and potassium bichromate, 100. Although it is hardly possible that any hydration takes place, it is found advisable to soak the zinc oxide in water for 24 hours before

the other reagents are added, the sulphuric acid after dilution being added gradually. Great care must be taken that the solutions are all cold, and the stirring is continuous, to avoid the pigment being deposited in a hard sandy form. Zinc yellows thus prepared are not liable to change during washing in a manner analogous to the lead compounds.

Zinc chrome is not much used, partly because it is expensive, partly because it cannot compete with the lead chromes in brilliance, depth of colour, and body. Still, owing to the fact that it can be mixed with sulphur pigments without change, it is often employed in the place of the lead chromes. Pure zinc chrome is completely soluble in sulphuric acid without any effervescence, but a slight effervescence may be disregarded. Any residue may be put down as adulteration, and its character can be ascertained by a few simple tests: it may be chrome yellow, barates, &c.

**GAMBOGE.**—Gamboge is a product of several trees of Eastern Asia: viz. *Garcinia Morella* var. *β. pedicellata* [*G. Hanburyi*], a native of Cambodia, the province of Chantibun in Siam, the islands on the east coast of the Gulf of Siam, and the south parts of Cochin China; *G. Morella*, growing in the moist forests of Ceylon and Southern India; and *G. pictoria*, of Southern India, by some considered identical with *G. Morella*. *G. travancorica*, of the southern forests of Travancore and the Tinnevelly Ghâts, is capable of affording small supplies of the pigment for local use, but not for export.

When the rainy season has set in, parties of natives start in search of gamboge-trees, and select those which are sufficiently matured. A spiral incision is made in the bark on two sides of the tree, and joints of bamboo are placed at the base of the incision so as to catch the gum-resin as it exudes with extreme slowness during a period of several months. It issues as a yellowish fluid, but gradually assumes a viscous and finally a solid state in the bamboo receptacle. It is very commonly adulterated with rice-flour and the powdered bark of the tree, but the latter imparts a greenish

tint. Sand is occasionally added. The product from a good tree may fill three bamboo joints, each 18 to 20 inches long and  $1\frac{1}{2}$  inches in diameter. The trees flourish on both high and low land. Annual tapping is said to shorten their lives, but if the gum-resin is only drawn in alternate years, the trees do not seem to suffer, and last for many years.

Dr. Jamie, of Singapore, who has gamboge-trees growing on his estate, says that they flourish most luxuriantly in the dense jungles. He considers the best time for cutting to be February to April. The filled bamboos are rotated near a fire till the moisture in the gamboge has evaporated sufficiently to permit the bamboo to be stripped from the hardened gum-resin. The gamboge is secreted by the tree chiefly in numerous ducts in the middle layer of the bark, besides a little in the dotted vessels of the outermost layer of the wood, and in the pith. It arrives in commerce in the form of cylinders, 4 to 8 inches long and 1 to  $2\frac{1}{2}$  inches in diameter, often more or less rendered shapeless. When good, it is dense, homogeneous, brittle, showing conchoidal fracture, scarcely translucent, and of rich brownish-orange colour. Inferior qualities show rough, granular fracture, and brownish hue, and are sometimes still soft. The pigment consists of a mixture of 15 to 20 per cent. gum with 85 to 80 per cent. resin. Its chief uses are in water-colour painting, and in varnishes.

KING'S YELLOW.—A familiar name for the trisulphide of arsenic, also known as orpiment (see p. 280).

NAPLES YELLOWS.—This group of pigments embraces several combinations of the oxides of lead and antimony, derived from various sources, and prepared by sundry methods. Two of the most useful formulæ are as follows:—

(a) Mix 3 lb. powdered metallic antimony, 1 lb. oxide of zinc, and 2 lb. red-lead; calcine, grind fine, and fuse in a closed crucible; grind the fused mass to fine powder, and wash well.

(b) Grind 1 part washed antimony with 2 parts red-lead

to a stiff paste with water, and expose to red heat for 4 or 5 hours.

There are a great many modifications both in the ingredients and the processes, and a great variety of shades in consequence.

Taken as a whole, the Naples yellows are unsatisfactory pigments, very prone to deteriorate in impure air, and necessitating great care in their preparation to avoid contact with iron, which turns them green. They cover well, are fairly brilliant, and mix readily with water or oil, but their application is declining rapidly.

OCHRES.—The large class of mineral pigments known collectively as ochres or sienna earths possess considerable importance, notably on account of their remarkable durability and their reasonable price. They all consist essentially of an earthy base coloured by oxide of iron or of manganese, or of both. Some authorities differentiate between ochres and siennas, and ascribe the latter name only to those earths which contain manganese, but this seems to be an arbitrary proceeding, because the term sienna, or more properly Siena, is derived solely from the name of the Italian province in which these minerals are worked. They are of widespread occurrence, both geographically and geologically, and the methods of mining and preparing them are not subject to much variation.

Consul Colnaghi, in his report on the mineral products of the province of Siena, says that Siena earths, known also under the names of ochre, bole, umber, &c., are considered by some mineralogists to be ferruginous clays, by others, minerals of iron. They are chiefly found in large quantities in the communes of Castel del Piano and Arcidosso. The yellow earths and bole found on the western slopes of Monte Amiata are true lacustrine deposits found amid the trachytic rocks, of which it is principally composed. They lie under, and are entirely covered by, the vegetable soil. Varying in compactness and colour, they are termed yellow

earths when of a clear ochreous tint, and *terra bolare*, or bole, when of a dark chestnut colour. Each deposit consists for the greater part of yellow earth, beneath which bole is found in strata or small veins. The mineral being very friable, its excavation is easy, and is generally conducted in open pits.

The different qualities are separated during the process, the bole, which has the higher commercial value, being the more carefully treated. After the first separation the bole is further classed into first, second, third, and intermediate qualities—*boletta*, *fascia*, *cerchione*, &c. Its most important characteristic is termed, in commercial language, *punto di colore*, or tint. The value of the bole rises as its tint deepens. Thus bole of the third quality is lighter than that of the second, and the second than that of the first. After the third quality comes the *terra guilla*. The yellow earths, after excavation, are exposed to the open air for about a year, by the pit side, without classification. The bole, on the contrary, is placed in well-ventilated storehouses to dry for about six months. This diversity of treatment is owing to the fact that exposure to the elements brightens the colour of the yellow earths, and raises their value, while it would damage the bole by turning its darker tint first into an orange yellow, and, if continued, into an ordinary yellow earth. It also loses in compactness and crumbles up under exposure.

In addition to the *punto di colore*, the size of the pieces influences the commercial value of the bole, which increases with their volume. Thus the classification is *bole pezzo*, *bole grapolino*, and *bole polvere*. The yellow earths are classed as *giallo in pezzo*, *giallo commune*, and *giallo impalpabile*, the impalpable being worth more than the common yellow. The production of the Siena earths is estimated at about 600 tons per annum, of which amount about 50 tons are calcined, and the rest sold in the natural condition. The value of the trade is estimated at from £4000 to £6000.

The European trade in these earths is very large. Rouen exports some 5000 tons yearly, and Havre about 1500 tons.

Similar deposits occur in America, where they are known as "paint-beds," and the earths are called "metallic paints." A prominent example is the paint-bed at Lehigh Gap, Carbon County, Pennsylvania, which was originally opened as an ironstone mine. The mineral proved valueless metallurgically, but remarkably useful as a pigment, since it contains about 28 per cent. of hydraulic cement, which hastens the drying and causes the paint to set without any addition of artificial dryers, thereby making it eminently fitted for all outdoor application.

Along the outcrop of the paint, the beds are covered by a cap or overburden of clay, and by the decomposed lower portion of the Marcellus slate, which is 50 feet thick at the Rutherford shaft.

Beginning with the Marcellus slate, the measures occur in the following descending order :—

- a. Hydraulic cement (probably Upper Helderberg), very hard and compact.
- b. Blue clay, about 6 inches thick.
- c. Paint-ore, varying from 6 inches to 6 feet in thickness.
- d. Yellow clay, 6 feet thick.
- e. Oriskany sandstone, forming the crest and southern side of the ridge.

East of the Rutherford shaft the sandstone forms the top-rock of the bed. This is due to an overthrow occurring between the Rutherford tunnel and shaft.

The paint-bed is not continuous throughout its extent. It is faulted at several places; sometimes it is pinched out to a few inches and again increases in width to 6 feet. A short distance south of Bowman's there is a fault striking north-east in the Marcellus slate, which has produced a throw of about 200 feet. The measures dip from  $10^{\circ}$  to  $90^{\circ}$ . The dip at the Rutherford shaft is about  $79^{\circ}$  south, whereas at

the tunnel it is 45° north. The ore is bluish-gray, resembling limestone, and is very hard and compact. The bed is of a lighter tint, however, in the upper than in the lower part, and this is probably due to its containing more hydraulic cement in the upper strata. The paint-ore contains partings of clay and slate at various places.

At the Rutherford shaft there are fine bands of ore, alternating with clay and slate, as follows—Sandstone (hanging-wall), clay, ore, slate, ore, clay, ore, clay, ore, slate, ore, cement, slate (foot-wall). These partings, however, are not continuous, but pinch out, leaving the ore without the admixture of clay and slate. Near the outcrop the bed becomes brown hematite, due to the leaching out of the lime and to complete oxidation. Occasionally, streaks of hematite are interleaved with the paint-ore. In driving up the breasts, towards the outcrop, the ore is found at the top in rounded, partially oxidised and weathered masses, called "bombshells," covered with iron oxide and surrounded by a bluish clay. In large pieces the ore shows a decided cleavage.

The method used in mining is a variation of panel-work. Nearly the same system of working is employed by all of the companies who have developed their mines either by means of tunnels or shafts. Tunnels are preferred whenever equally convenient, because they involve no expenses for pumping and hoisting machinery, fuel, repairs to machinery, &c.

The following description of the operation of the Rutherford mines is typical of all the workings in the vicinity.

The Rutherford tunnel is 6 feet high and 600 feet long. The gangways are driven along the foot-wall of the cement side, 6 feet high, and are heavily timbered and lagged at the top and on the clay side. The sets of timbers are  $3\frac{1}{2}$  feet apart, and usually of 9-inch timber. The width at the top is  $3\frac{1}{2}$  feet, with a spread of 5 feet at the bottom, the extra width being cut from the clay. Where the cement-rock is

firm, the collar is hitched 6 inches into it and supported by a leg on the clay side. The cost of the timber is 54 cents (2s. 3d.) per set, including the lagging. The monkey gangway, which carries the air along the top of the breast from the air-shaft, is  $2\frac{1}{2}$  feet high,  $1\frac{1}{2}$  feet wide at the top, with a spread of  $2\frac{1}{2}$  feet at the bottom. Wooden rails with a gauge of 18 inches are spiked to the cross-ties.

The gangway is not driven continuously, but after being driven about 55 feet on either side of the shaft, the breasts are started 25 feet from the shaft, a pillar being left to protect it. The breast is then opened up to the face of the gangway, and when one ore-breast is worked out, the gangway is driven ahead about 30 feet, and a new breast is opened and worked out before commencing a third. The air-hole is first driven to the surface, then the breast is opened to its full width of 6 feet. The thickness of the bed of ore here varies from 4 to 6 feet, depending upon the thickness of the partings of clay and slate. The clay and slate are left on the bottom, which is made sloping to allow the ore to roll down to the shute; this is 6 feet wide and 4 feet long and heavily timbered. Small props or sprags are hitched into the cement, and wedged with a lid on the clay side to prevent falls of rock.

The holes are drilled by hand in the clay-partings. They vary in depth from 1 to 4 feet, and the charge of dynamite is varied correspondingly, according to the amount of ore it is desired to throw down. The loose ore is wedged down with crowbars and picks, and is then freed from any adhering clay and thrown down the shute. It is there loaded into boxes holding about half a ton each, which are pushed to the shaft on a truck. The ore-boxes have four rings at the corners, to which are attached four chains, suspended from the wire hoisting-rope. At the top of the shaft the boxes are detached and placed on a truck, which is run to the dump. Thirty cars, averaging 15 tons, are extracted in a day of two shifts, the day-shift working nine hours and the

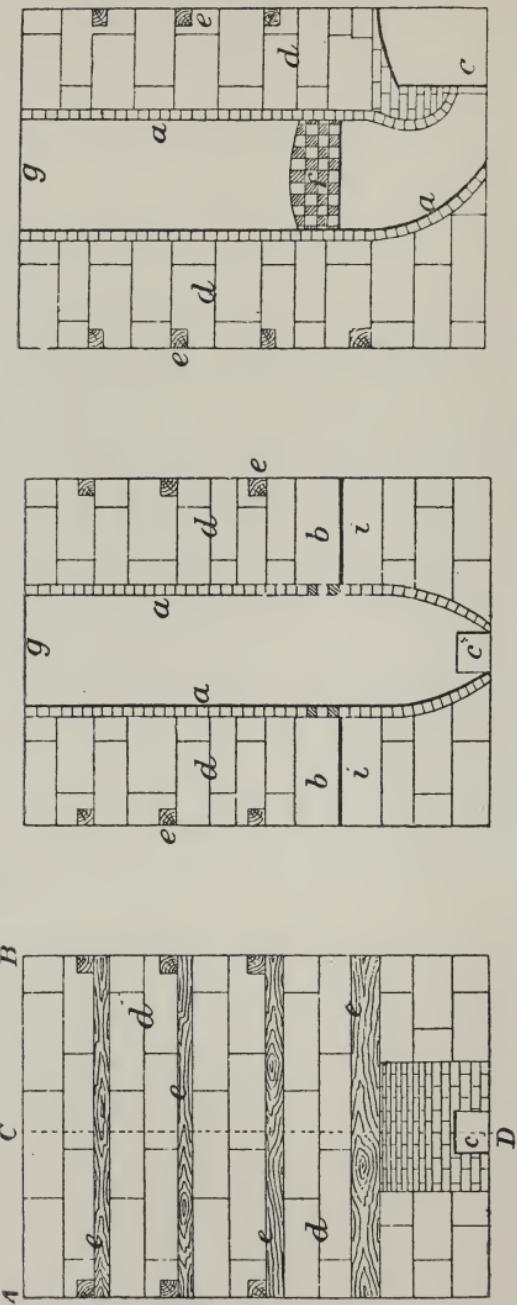
night-shift eleven. The pay of the miners is 5s. per shift. The cost of mining the ore averages 7s. per ton.

The ore, as it comes from the mines, is free from refuse, great care having been taken to separate slate and clay from it in the working places. It is hauled in 2-ton wagons to kilns, which are situated on a hill-side for convenience in charging. The platform upon which the ore is dumped is built from the top of the kiln to the side of the hill. The ore is first spalled to fist-size and freed from slate, and is then carried in buggies to the charging-hole of the kiln.

The slate, when burned, has a light yellowish colour, which would change the colour of the product. Figs. 30 to 32 represent a front elevation of the kiln and two sections at right angles to each other. The kiln is 22 feet high and 16 feet square on the outside. The interior is cylindrical, 5 feet in diameter, with a fire-brick lining *a* of the best quality. The interior lining slopes from the fire-place *b* to the door *c*, by which the charges are withdrawn; this facilitates the removal of the calcined ore. The casing *d* is of sandstone,  $5\frac{1}{2}$  feet thick, and tied together with the best white-oak timber *e*. When charged, a kiln holds 16 tons of ore, and the kiln is kept constantly full. The heat passes from the fire-places *b*—of which there are two, placed diametrically opposite each other—through a checker-work *f* of brick into the centre of the charge. The charge enters at *g* and is withdrawn by a door *c* in the front wall, 2 feet long and 18 inches high. The ashpit is at *i*. The fire is kept at a cherry-red heat, and about one cord of wood is burned every twenty-four hours.

The kiln works continuously, calcined ore being withdrawn and fresh charges made without interruption. The ore is subjected for forty-eight hours to the heat, which expels the moisture, sulphur and carbon-dioxide. About  $1\frac{1}{2}$  tons of calcined ore are withdrawn every three hours during the day. The outside of the lumps of calcined ore has a light brown colour, while the interior shows upon fracture a darker brown. Great care is necessary to regulate the heat

so that the ore is not over burned. When this happens, the product has a black scoriaceous appearance, and is unfit



Figs. 30, 31, 32.—RUTHERFORD AND BARCLAY KILN.

for the manufacture of metallic paint, as it is extremely hard to grind.

The calcined ore is carried from the kiln in wagons to the mill, where it is broken to the size of grains of corn in a rotating crusher. The broken ore is carried by elevators to the stock-bins at the top of the building, and thence by shutes to the hoppers of the mills, which grind it to the necessary degree of fineness. Elevators again carry it to the packing-machine by a spout, and it is packed into barrels holding 500, 300, or 100 lb. each.

*Characters.*—Ochres owe their colour to hydrated oxide of iron, besides which body they contain clayey matter (silicate of alumina), earthy matters, barytes, carbonate and sulphate of calcium, &c., dependent upon the locality from whence they are obtained; thus Derbyshire ochres contain mostly calcareous earthy matters, barytes, gypsum, &c., while Oxford ochres and French ochres contain clayey matter; Welsh ochres are variable, and usually contain a good deal of silicious matter.

Crude ochres should first be assayed for actual colouring matter and grit or refuse. This can be done by a kind of levigation method: 200 grains of the crude ochre are crushed in a mortar; the grinding must not be too well done, or otherwise faulty results will be obtained. The crushed ochre is put into a tall conical glass; a long glass funnel passes to the bottom of the glass, and the whole is arranged in a large glass basin or dish. A current of water is now caused to flow down the glass funnel; this washes the fine particles of ochre away from the grit, and they are carried over the sides of the glass into the dish. Here they are allowed to settle, and are collected and weighed after drying, an operation which gives the amount of ochre in the crude material.

Levigated and prepared ochres can be tested for colour and covering power, by the usual methods. These are the most important points about ochres to which attention should be paid.

ORPIMENT.—Orpiment, king's yellow, or trisulphide of arsenic, is a lemon or orange-yellow coloured substance, found native in Hungary, the Hartz, and other places. The finest samples used by artists (golden orpiment) come from Persia. The commercial article is artificially prepared for use as a pigment in the following way:—

A mixture of arsenious acid and sulphur is placed in an iron subliming-pot, similar to those used in the preparation of crude white arsenic. The mixture is then heated until the sublimate which immediately forms upon the rings fixed above the pot begins to melt. The proportions of the two ingredients used vary largely, the best colours being probably produced when the mixture contains from one-third to one-fifth of sulphur; for the lighter colours, a smaller proportion of sulphur is employed. Orpiment made in this manner consists of a mechanical mixture of sulphide and oxide of arsenic.

Orpiment is also employed as a dye, in the preparation of fireworks, and in some depilatories. The native sulphide is preferred to the artificial variety by artists and dyers, by reason of its richer colour; but it is a colour which in reality is hardly ever used now. Sometimes it is employed in water-colours, but as a pigment it is worthless. If it comes in contact with white lead it is decomposed in time, and a brown or black sulphide of lead is formed. While it endures it is a very brilliant colour.

REALGAR.—Realgar or disulphide of arsenic, is a deep orange-red substance, soluble in water, and highly volatile and poisonous. It is found native in some volcanic districts, especially in the neighbourhood of Naples; but the commercial article is made by distilling, in earthenware retorts, arsenical pyrites, or a mixture of sulphur and arsenic, or of orpiment and sulphur, or of arsenious acid, sulphur, and charcoal, in the proper proportions; it has not the brilliant colour of the native mineral, and is much more poisonous.

On a large scale, the manufacture is carried on in the

following way:—The ingredients are mixed together in such proportions that the mixture shall contain 15 per cent. of arsenic, and from 26 to 28 per cent. of sulphur, in order to make allowance for the volatilisation of a portion of the latter substance. The mixture is then placed in a series of earthenware retorts, which are charged every twelve hours with about 60 lb.; this quantity should fill them three parts full. These are then gradually heated to redness for from eight to twelve hours, during which time the realgar distils off, and is collected in earthen receivers, similar to the retorts, but perforated with small holes to permit the escape of these gases. After the operation, the receivers are emptied, and the crude product is remelted. This is performed in cast-iron pots, the contents being well agitated, and the slag carefully removed. The requisite amount of sulphur or arsenic is then added, according to the colour of the mixture, or else a proper quantity of realgar containing an excess of the required constituent, and the mass is again stirred. When, on cooling, it exhibits the correct colour and compactness, it is run off into conical moulds of sheet iron, cooled and broken up; it is sometimes refined by re-sublimation. The chief use of realgar is as a pigment; and in pyrotechny in the preparation of white fires.

As a pigment it possesses the same features and faults as its close ally orpiment.

SIENNAS.—Another name for ochres, described on p. 272.

## CHAPTER IX.

## LAKES.

ORGANIC colouring matters for use as pigments are mostly made in the form of "lakes," by one of the three following methods :—

(a) To a filtered solution of the colouring matter is added a solution of alum ; the whole is agitated, and the colour is precipitated by a solution of carbonate of potash.

(b) A solution of the colouring matter is made in a weak alkaline lye, and precipitated by adding a solution of alum.

(c) Recently-precipitated alumina is agitated with a solution of the colouring matter as before, until the liquid is nearly decolorised, or the alumina assumes a sufficiently deep tint. The first method is generally adopted for acidulous solutions of colouring matter, or those injured by alkalies ; the second for those not injured by alkalies ; the third, for those whose affinity for gelatinous alumina enables them to combine with it by mere agitation.

Alumina in a state suitable for the preparation of the pigments known as "lakes" may be produced in the following manner :—Dissolve 1 lb. of alum in  $\frac{1}{2}$  gallon of water, and add 75 grains of sulphate of copper, and about  $\frac{1}{4}$  lb. of zinc turnings ; leave the mixture for three days in a warm place, renewing the water lost by evaporation. The copper is first deposited upon the zinc, the two metals thus forming a voltaic couple sufficiently strong. Hydrogen is disengaged, sulphate of zinc is formed, and the alumina gradually separates in the state of a very fine powder ; the action is

allowed to continue until there is no more alumina left in solution, or until ammonia ceases to give a precipitate. If the reaction is prolonged beyond this point, oxide of iron will precipitate if present. The alumina washes easily, and does not contract upon drying.

BRAZIL-WOOD LAKE.—(a) Digest 1 lb. ground Brazil-wood in 4 gal. water for 24 hours, boil  $\frac{1}{2}$  hour, and add  $1\frac{1}{2}$  lb. alum dissolved in a little water; mix, decant, strain, add  $\frac{1}{2}$  lb. tin solution, again mix well, and filter; to the clear liquid cautiously add a solution of carbonate of soda while a precipitate forms, avoiding excess; collect, wash, and dry. The shade will vary according as the precipitate is collected.

(b) Add washed and recently-precipitated alumina to a strong filtered decoction of Brazil-wood.

CARMINATED LAKE.—(a) The cochineal residue left in making carmine is boiled with repeated portions of water till exhausted; the liquor is mixed with that decanted off the carmine, and at once filtered; some recently-precipitated alumina is added, and the whole is gently heated, and well agitated for a short time. As soon as the alumina has absorbed enough colour, the mixture is allowed to settle, the clear portion is decanted, and the lake is collected on a filter, washed, and dried. The decanted liquor, if still coloured, is treated with fresh alumina till exhausted, and thus a lake of second quality is obtained.

(b) To the coloured liquor obtained from the carmine and cochineal as just stated, a solution of alum is added, the filtered liquor is precipitated with a solution of carbonate of potash, and the lake is collected and treated as before. The colour is brightened by addition of tin solution.

CARMINE.—Boil 1 lb. cochineal and 4 dr. carbonate of potash in  $7\frac{1}{2}$  gal. water for  $\frac{1}{4}$  hour. Remove from the fire, and stir in 8 dr. powdered alum, and allow to settle for 20 to 30 minutes. Pour the liquid into another vessel, and mix in a strained solution of 4 dr. isinglass in 1 pint water; when a skin has

formed upon the surface, remove from the fire, stir rapidly, and allow to settle for  $\frac{1}{2}$  hour, when the deposited carmine is carefully collected, drained, and dried.

COCHINEAL LAKE.—(a) Digest 1 oz. coarsely powdered cochineal in  $2\frac{1}{2}$  oz. each water and rectified alcohol for a week; filter, and precipitate by adding a few drops of tin solution every 2 hours, till the whole of the colouring matter is thrown down; wash the precipitate in distilled water, and dry.

(b) Digest powdered cochineal in ammonia water for a week; dilute with a little water, and add the liquid to a solution of alum as long as any precipitate (lake) falls.

(c) Boil 1 lb. coarsely powdered cochineal in 2 gal. water for 1 hour; decant, strain, add solution of 1 lb. cream of tartar, and precipitate with solution of alum. By adding the alum first and precipitating the lake with the tartar, the colour is slightly changed.

MADDER LAKE.—(a) Tie 2 oz. madder in a cloth, beat it well in a pint of water in a stone mortar, and repeat the process with about 5 pints of fresh water till it ceases to yield colour; boil the mixed liquor in an earthen vessel, pour into a large basin, and add 1 oz. alum dissolved in 1 pint boiling water; stir well, and gradually pour in  $1\frac{1}{2}$  oz. of strong solution of carbonate of potash; let stand until cold, pour off the yellow liquor from the top, drain, agitate the residue repeatedly in 1 qt. boiling water, decant, drain, and dry.

(b) Add a little solution of acetate of lead to a decoction of madder, to throw down the brown colouring matter; filter, add solution of tin or alum, precipitate with solution of carbonate of soda or potash, and proceed as before.

(c) Macerate 2 lb. ground madder in 1 gal. water for 10 minutes; strain and press quite dry; repeat a second and third time, and add to the mixed liquors  $\frac{1}{2}$  lb. alum dissolved in 3 qt. water; heat in water-bath for 3–4 hours, adding water as it evaporates; filter first through flannel, and when

cold enough through paper; add solution of carbonate of soda as long as precipitate falls; wash the latter till the water comes off colourless, and dry.

YELLOW LAKES.—(a) Boil 1 lb. Persian berries, quercitron-bark, or turmeric, and 1 oz. cream of tartar, in 1 gal. water till reduced to half; strain the decoction, and precipitate by solution of alum.

(b) Boil 1 lb. of the dyestuff with  $\frac{1}{2}$  lb. alum in 1 gal. water, and precipitate by solution of carbonate of potash.

(c) Boil 4 oz. annatto and 12 oz. pearlash in 1 gal. water for  $\frac{1}{2}$  hour; strain, precipitate by adding 1 lb. alum dissolved in 1 gal. water till it ceases to produce effervescence or a precipitate; strain and dry.

For information concerning the numerous coal-tar colours now largely manufactured into lakes, the reader is referred to "Spon's Encyclopædia of Industrial Arts."

## CHAPTER X.

## LUMINOUS PAINTS.

THE luminosity of minerals has an obvious practical value in the case of such substances as can be conveniently applied in the form of a paint to surfaces which are alternately exposed to light and darkness, such exposed surfaces emitting at one time the light which they have absorbed at another. Familiar illustrations are street plates, buoys, and interiors of railway carriages having to traverse many tunnels. The light absorbed may be either daylight or powerful artificial light. With this object, several compositions are prepared under the generic name of luminous paints. They are chiefly as follows :—

(1) Balmain's.—This consists of a phosphorescent substance introduced into ordinary paint. The phosphorescent substance employed for the purpose is a compound obtained by simply heating together a mixture of lime and sulphur, or substances containing lime and sulphur, such as alabaster, gypsum, &c., with carbon or other agent, to remove a portion of the oxygen present; or by heating lime in a vapour containing sulphur. In applying this phosphorescent powder, the best results are obtained by mixing it with a colourless varnish made from mastic and turpentine; drying oils, gums, pastes, sizes, &c., may, however, also be used.

(2) A French compound.—100 lb. of a carbonate of lime and phosphate of lime produced by the calcination of sea-shells, and especially those of the genus *Tridacna* and the cuttle-fish bone, intimately mixed with 100 lb. of lime rendered chemically pure by calcination, 25 lb. of calcined

sea-salt, 25-50 per cent. of the whole mass of sulphur, incorporated by the process of sublimation, and 3-7 per cent. of colouring matter in the form of powder composed of mono-sulphide of calcium, barium, strontium, uranium, magnesium, aluminium, or other mineral or substance producing the same physical appearances, *i. e.* which, after having been impregnated with light becomes luminous in the dark. After having mixed these five ingredients intimately, the composition obtained is ready for use. In certain cases, and more especially for augmenting the intensity and the duration of the luminous effect of the composition, a sixth ingredient is added, in the form of phosphorus reduced to powder, which is obtained from seaweed by the well-known process of calcination. As to proportion, it is found that the phosphorus contained in a quantity of seaweed, representing 25 per cent. of the weight of the composition formed by the five above-named ingredients, gives very good results.

The phosphorescent powder thus obtained and reduced to paste by the addition of a sufficient quantity of varnish, such as copal, may serve for illuminating a great number of objects, by arranging it in more or less thick coatings, or by the application of one or more coatings of the powder incorporated in the varnish, or by varnishing previously and sprinkling the dry powder upon the varnish. The amount of powder applied should not exceed the thickness of a thin sheet of cardboard.

The dry phosphorescent powders are also converted into translucent flexible sheets of unlimited length, thickness, and width, by mixing them with about 80 per cent. of their weight of ether and collodion in equal parts in a close vessel, and rolling the product into sheets, with which any objects may be covered which are intended to be luminous in the dark. The powders may also be intimately mixed with stearine, paraffin, rectified glue, isinglass, water glass, or other transparent solid matter, in the proportion of 20 to 30 per cent. of the former with 50 to 80 per cent. of either of

these substances, and this mass is then reduced into sheets of variable length, width, and thickness, according to their intended applications. A luminous glass is also manufactured by means of the powders, by mixing them in glass in a fused state in the proportions of 5 to 20 per cent. of the mass of glass. After the composition has been puddled or mixed, it is converted into different articles, according to the ordinary processes; or after the manufacture of an object still warm and plastic, made of ordinary glass, it is sprinkled with the powders, which latter are then incorporated into the surface of the article by pressure exerted in the mould, or in any other suitable way.

It has been observed, after various trials, that the passage of an electric current through the different compositions augments their luminous properties or brilliancy to a great extent; this peculiarity is intended to be utilised in various applications too numerous to describe, but of which buoys form a good example. The current of electricity is furnished by plates of zinc and copper mounted on the buoy itself, when the latter is used at sea; but in rivers and fresh-water inlets the battery will be carried in the interior of the buoy. To secure the full effect, 10 to 20 per cent. of fine zinc, copper, or antimony dust is added to the phosphorescent powder described.

(3) Take oyster-shells and clean them with warm water; put them into the fire for  $\frac{1}{2}$  hour; at the end of that time take them out and let them cool. When quite cool, pound them fine, and take away any grey parts, as they are of no use. Put the powder in a crucible with alternate layers of flowers of sulphur. Put on the lid, and cement with sand made into a stiff paste with beer. When dry, put over the fire and bake for an hour. Wait until quite cold before opening the lid. The product ought to be white. You must separate all grey parts, as they are not luminous. Make a sifter in the following manner:—Take a pot, put a piece of very fine muslin very loosely across it, tie around

with a string, put the powder into the top, and rake about until only the coarse powder remains; open the pot, and you will find a very small powder. Mix it into a thin paint with gum water, as two thin applications are better than one thick one. This will give paint that will remain luminous far into the night, provided it is exposed to the light during the day.

(4) Sulphides of calcium, of barium, of strontium, &c., give phosphorescent powders when duly heated. Each sulphide has a predominant colour, but the temperature to which it is heated has a modifying effect on the colour. Calcine in a covered crucible, along with powdered charcoal, sulphate of lime, sulphate of baryta, or sulphate of strontia; there is produced in each case a greyish white powder, which, after exposure to strong light (either sun-light or magnesium light), will be phosphorescent, the colour depending on the sulphate used and the degree of heat employed.

(5) Five parts of a luminous sulphide of an alkaline earth, 10 of fluorspar, cryolite, or other similar fluoride, 1 of barium borate; powdered, mixed, made into a cream with water, painted on the glass or stone article, dried, and fired in the usual way for enamels. If the article contains an oxide of iron, lead, or other metal, it must be first glazed with ground felspar, silica, lime phosphate, or clay, to keep the sulphur of the sulphide from combining with the metal. The result is an enamelled luminous article. (Heaton and Bolas.)

(6) Boil for 1 hour  $2\frac{1}{4}$  oz. caustic lime, recently prepared by calcining clean white shells at a strong red heat, with 1 oz. pure sulphur (flowers) and 1 qt. soft water. Set aside in a covered vessel for a few days; then pour off the liquid, collect the clear orange-coloured crystals which have deposited, and let them drain and dry on bibulous paper. Place the dried sulphide in a clean graphite crucible provided with a cover. Heat for  $\frac{1}{2}$  hour at a temperature just

short of redness, then quickly for about 15 minutes at a white heat. Remove cover, and pack in clay until perfectly cold. A small quantity of pure calcium fluoride is added to the sulphide before heating it. It may be mixed with alcoholic copal varnish. (*Boston Jl. Chem.*)

The luminous calcic sulphide (also called sulphide of calcium), now obtainable in the market, has a yellowish white tint, which considerably limits its direct application as a paint. On the other hand, the calcic sulphide, or the luminous paint obtained therefrom, loses its luminous property, if it is directly mixed with the ordinary commercial paints.

Schatté, of Dresden, produces durable white or coloured paints, containing a luminous substance which causes them to shine in the dark, without changing or neutralising in daylight the tint of the colouring substance or substances contained in such paints.

For this purpose, Zanzibar or cowrie copal is melted over a charcoal fire, 15 parts of this melted mass are dissolved in 60 parts of French turpentine, and the resulting mixture is filtered, whereupon 25 parts of pure linseed oil are added, which linseed oil has been previously boiled and allowed to cool a little. The lake varnish thus obtained is carefully treated in a paint mill with granite rollers, and worked into a luminous paint by one of the processes hereinafter described.

Iron rollers capable of giving off under great pressure small particles of iron, which might affect the luminous power, should not be used. Lake varnish as obtained in commerce contains nearly always lead or manganese, which would destroy the luminous power of the calcic sulphide.

The proportions given are as follows :—

*Pure White* : By mixing 40 parts of lake varnish obtained as described with 6 parts of prepared baric sulphate, 6 parts of prepared calcic carbonate, 12 parts of prepared zinc sulphide white, and 36 parts of calcic sulphide in a luminous

condition, in an oil vessel, and worked into a coarse emulsion, which is then ground fine between the rollers.

*Red*: 50 parts of the said lake varnish are mixed with 8 parts of prepared baric sulphate, 2 parts of prepared madder lake, 6 parts of prepared realgar (diarsenious disulphide), and 34 parts of calcic sulphide in a luminous condition, and the mixture is worked in the same way as described for white.

*Orange*: 46 parts varnish are mixed with 17·5 parts prepared barium sulphate, 1 part prepared India yellow, 1·5 parts prepared madder lake, and 38 parts luminous calcium sulphide.

*Yellow*: 48 parts varnish are mixed with 10 parts prepared barium sulphate, 8 parts barium chromate, and 34 parts luminous calcium sulphide.

*Green*: 48 parts varnish are mixed with 10 parts prepared barium sulphate, 8 parts chromium oxide green, and 34 parts luminous calcium sulphide.

*Blue*: 42 parts varnish, 10·2 parts prepared barium sulphate, 6·4 parts ultramarine blue, 5·4 parts cobalt blue, and 46 parts luminous calcium sulphide.

*Violet*: 42 parts varnish, 10·2 parts prepared barium sulphate, 2·8 parts ultramarine violet, 9 parts cobalt arsenate, and 36 parts luminous calcium sulphide

*Grey*: 45 parts of the varnish are mixed with 6 parts prepared barium sulphate, 6 parts prepared calcium carbonate, 0·5 part ultramarine blue, 6·5 parts grey zinc sulphide.

*Yellowish-brown*: 48 parts varnish, 10 parts precipitated barium sulphate, 8 parts auripigment, and 34 parts luminous calcium sulphide.

Luminous colours for artists' use are prepared by using pure East India poppy oil, in the same quantity, instead of the varnish, and taking particular pains to grind the materials as fine as possible.

For luminous oil-colour paints, equal quantities of pure

linseed oil are used in the place of the varnish. The linseed oil must be cold-pressed and thickened by heat.

All the above luminous paints can be used in the manufacture of coloured papers, &c., if the varnish is altogether omitted, and the dry mixtures are ground to a paste with water.

The luminous paints can also be used as wax colours for painting on glass and similar objects, by adding, instead of the varnish, 10 per cent. more of Japanese wax and one-fourth the quantity of the latter of olive oil. The wax colours prepared in this way may also be used for painting upon porcelain, and are then carefully burned without access of air. Paintings of this kind can also be treated with water glass.

## CHAPTER XI.

### EXAMINATION OF PIGMENTS.

BESIDES the chemical tests for purity and adulteration, which necessarily must vary with each pigment, there are certain other examinations which partake rather of a mechanical nature, and which are applicable to practically all pigments without any modification. They are directed chiefly to ascertaining fineness, body, colour, and durability.

**FINENESS.**—Fineness may be tested for as follows:—A tall glass cylinder is filled with clean water, and about  $\frac{1}{2}$  oz. of the pigment under examination is well shaken in the water; the glass is placed on one side to settle out, and the length of time taken to settle may be noted for future reference. The finer the sample, the longer the time it takes to settle out; and the time in seconds may be taken as an approximate estimate of the fineness of the sample.

**BODY OR COVERING POWER.**—An equal and exact quantity, say 50 gr., of the sample under examination and of a standard sample of the same degree of fineness is weighed out, and placed on two separate sheets of paper. To each sample is added an equal quantity, say 15 gr., of vegetable black or of very finely ground barytes, according as the pigment is a light or a dark-tinted kind. The ingredients of each sample are most intimately and completely mixed, and the tints of the two mixtures are compared by observation with the naked eye. The pigment which most nearly retains its own colour, possesses the greatest body or covering power.

**COLOUR.**—The colour or tint of a pigment can only be

estimated by comparing it with a standard sample ; this is done as follows :—A sheet of black paper, with a dead surface, is spread out on a table in front of a window, a small heap of the standard is placed on the paper, and next to it a similar heap of the sample to be compared ; by means of a palette knife the surface of the two heaps is flattened out ; on now carefully looking at the two heaps, the one which has the purest colour can readily be picked out. The heaps should be looked at from several points of view before a final judgment is arrived at. If the pigment is dark-coloured, it should be spread on white paper, taking care that the same kind of paper is used for the two samples.

**DURABILITY.**—Durability is not a difficult point to test, but it takes some time to make a complete test. The best method is to mix a small quantity of the pigment in question with raw linseed oil, cover a piece of glass with the mixture, and expose it outside to the action of the sun and air for some time, noting at intervals how it behaves. It is well for the sake of comparison to coat a second piece of glass with the mixture, and keep this in a dark place. The difference between the two from time to time will show how the pigment behaves under the influence of light and air. As the durability of pigments is decidedly different according as they are used in oil or water-colour painting, the oil in the former case acting as a protective agent, it is well to use a similar test, using a little gum water as a vehicle to mix the pigment with. It will take from two to three months at least to properly test the durability of a pigment in summer, while in winter the time will be increased considerably. Glass is the best substance to use, as it is quite neutral, and does not of itself introduce into the test any injurious element, as wood or paper might do, although these bodies may be used if thought desirable.

## CHAPTER XII.

## VEHICLES AND DRYERS.

PAINT consists essentially of two parts, the pigment (see Chapters I. to VIII.), and the vehicle or medium. In the case of oil paints, a third substance termed a dryer becomes necessary, to facilitate the "drying," or solidification of the vehicle.

A perfect vehicle should mix readily with the pigment, forming a mass of about the consistency of treacle. It should itself be colourless, and have no chemical action upon the pigments with which it is mixed. When spread out in a thin layer upon a non-porous substance, it should solidify, and form a film not liable to subsequent disintegration or decay, and sufficiently elastic to resist a slight concussion.

Unfortunately, we possess no vehicle which complies with all these conditions; those which most nearly approach them are the drying oils. Oils are compound bodies containing acids and a base. Some oils oxidise very rapidly, while others do not oxidise at all. When oils oxidise they change their colour, and however white they may be at first, they gradually turn yellow and finally brown. The advantages of oils are that they mix kindly with most pigments, can be dissolved in turpentine, and can be used in almost any desired state of fluidity. Against these have to be set the disadvantage of the oxidation of the oil, to which oxidation the use of oil in paint is entirely due.

The use of oil in painting is said to have been invented in the 14th century, and, in a short time, it reached a considerable degree of perfection. We have only to compare a Van

Eyck with a painting by a modern master—Turner, for instance—to see that even the best of recent painters have not succeeded in giving to their works that durability which the originators of the method attained. All organic substances are liable to a more or less rapid oxidation, especially if exposed to light and heat. Oil is no exception to this rule; but it seems that, in its pure state, it is much more durable than when mixed with other substances. Although ground-nut- and poppy-oils are sometimes employed by artists where freedom from colour is essential, yet linseed-oil is the vehicle of by far the larger proportion of paints used both for artistic and general purposes.

Oil-paint appears to have been unknown to the ancients, who used various vehicles, chiefly of animal origin. One of these, which was in high repute at Rome, was the white of eggs beaten with twigs of the fig-tree. No doubt the india-rubber contained in the milky juice exuding from the twigs contributed to the elasticity of the film resulting from the drying of this vehicle. Pliny was aware of the fact that when glue is dissolved in vinegar and allowed to dry, it is less soluble than in its original state. Many suggestions have been made in modern times for vehicles in which glue or size plays an important part. In order to render it insoluble, various chemicals have been added to its solution, such as tannin, alum, and a chromic salt. None of these vehicles, however useful for special purposes, has become sufficiently well known to warrant description here.

Substitutes which do claim attention are wax and dammar gum, or paraffin wax, dissolved in turpentine. The colours must then be ground in turpentine and not in oil. Such a vehicle is very pleasant to work with, and gives good results; moreover, it permits alterations or corrections to be made by rubbing out with turpentine. Nevertheless, both the wax and the turpentine undergo oxidation to some extent, and are therefore not altogether free from the same objections as oils. But benzol, especially when carefully

prepared, answers all the purposes of turpentine without undergoing oxidation. The only drawback that can be urged against benzol is its odour, which some people have an aversion to; but it really has very little smell, and it evaporates away completely in a very short time. A mixture of wax, dammar, and benzol forms an excellent vehicle. The wax may be replaced by paraffin wax with advantage.

It is desirable to be able to ascertain whether the oil intended for use is, or is not, adulterated with non-drying oil. The distinction of non-drying oils is that they solidify when acted upon by peroxide of hydrogen, or by sub-nitrate of mercury—the oleic acid is concreted, and a substance called elaidin is formed. This does not take place with the drying oils.

The oils used in paint making are chiefly—

Ground-nut.	Poppy-seed.
Hempseed.	Tobacco-seed.
Kukui or candle-nut.	Walnut.
Linseed.	Wood or Tung.
Meuhaden.	

GROUND-NUT OIL.—The ground-nut or pea-nut (*Arachis hypogaea*) is very widely cultivated in the tropics for the sake of its oily seeds. In Java, the oil is extracted by drying the seeds in the sun, and then subjecting them to pressure. In European mills, the nuts are first cleaned, then decorticated and winnowed, by which the kernels are left perfectly clean. These are crushed like any other oil seed, and put into bags, which are introduced into cold presses; the expressed oil is refined by passing through filter-bags. The residual cake is ground very fine, and pressed under 3 tons to the inch, in the presence of steam-heat; this affords a second quantity of oil, inferior in quality to the cold pressed. The usual product is 1 gal. of oil from 1 bush. of nuts by the cold process, besides the extra yield by the hot pressing. In

France, where the oil is most largely prepared, three expressions are adopted, as with some sorts of gingelly: the first gives about 18 per cent. of superfine oil, fit for alimentary purposes; the second, after moistening with cold water, affords 6 per cent. of a fine oil, suitable for lighting and for woollen-dressing; the third, after treating with hot water, yields 6 per cent. of *rabat*, or oil applicable only to soap-making. In India, the total mean yield is 37 per cent. at Pondicherry, and 43 in Madras.

The cold-pressed oil is almost colourless, of agreeable faint odour, and bland olive-like flavour. The best has a sp. gr. of about 0·918, or 0·9163 at 59° F.; it becomes turbid at 37½° F., concretes at 26½°–25° F., and hardens at 19½° F. By exposure it changes very slowly, but thickens with time, and assumes a rancid odour and flavour. It is not a good oil for paint.

**HEMPSEED-OIL.**—The seeds of the hemp plant, so well-known as a fibre-producer, are valued for their oil. It is from Russia and Lorraine that the seed for expressing mostly comes. When the fibrous stems are tied in bundles, the seed is rudely threshed out, and spread in thin layers under cover to dry. The extraction of the oil is performed in the same manner as with other seed oils, described on p. 308. The proportion of oil contained in the seed is about 34 per cent. on an average; the yield varies from 25 to 30 per cent. The oil is at first greenish or brownish-yellow, deepening with exposure to the air; the flavour is disagreeable, and the odour is mild. It has a sp. gr. of 0·9252 at 59° F.; it thickens at 5° F., and solidifies at – 13° to – 18° F.; it dissolves in 30 parts of cold alcohol and any proportion of boiling; it saponifies with difficulty, forming a soft soap, but less soft than that from linseed oil. It is inferior for the painter's purposes.

**KUKUI OR CANDLE-NUT OIL.**—An oil bearing a multitude of names is obtained from the candle-nut (*Aleurites moluccana*). It is the most important product of the tree, and constitutes about two-thirds of the entire weight of the

kernel of the nut. A great obstacle to its wider development is the difficulty encountered in extracting the kernels from the shells, both on account of the extreme hardness of the latter, and the obstinacy with which the two adhere. Boiling is out of the question, as the kernels are cooked long before the shells are affected ; but there is every reason to suppose that a slight roasting would have the desired effect, inasmuch as this plan seems to be adopted successfully by the Samoans. The weight of the shells necessitates this treatment being performed on the spot, and, as the kernels quickly become rancid and dark-coloured after liberation, they must also be operated upon without removal. The local cheapness of labour is an additional argument in favour of preparing the oil at the places where the nut grows. The extraction of the oil is very simple. In Jamaica, Polynesia, and the East Indies, 50 per cent. is obtained by boiling the kernels in water ; by reducing the kernels to meal, heating in a water-bath, and placing the mass in bags under hydraulic pressure, the yield is about 60–66 per cent. The shells are themselves excellent fuel. The oil is completely clarified by mere filtration. As ordinarily prepared, it is amber-coloured, tasteless and odourless ; slightly viscid at the temperature of the air in England, congealing at 32° F. ; its sp. gr. is 0.923 ; it is insoluble in alcohol, and saponifies readily, giving a very soft soda-soap. It dries less rapidly than linseed oil, and is used for mixing paints and making oil-varnishes. It is said to corrode tin plate and even platinum.

**LINSEED-OIL.**—The flax plant, so well known as yielding a textile fibre, affords a valuable oil-seed. The supplies of linseed for crushing are furnished chiefly by Russia and India. It is found that, as a general rule, the colder the climate in which the seed is grown, the greater are the drying properties of the oil, but the worse is its colour. In India, preference is given to white seed, as yielding 2 per cent. more oil, affording

it more freely, and giving a softer and sweeter cake, than the red seed ; the latter, moreover, always comes to market largely mixed with rape-seed, which is very difficult of separation, and greatly depreciates the market value. Oil from unripe seed is watery. The seed should always be kept for 3-4 months in a dry place, as the oil furnished after this lapse of time is much more abundant than when the expression takes place immediately after the harvest. The seed is crushed and pressed in the manner described on p. 308. The best and finest oil is that which is "cold-drawn"; it is paler, less odorous, and less flavoured, but the yield is only 21-22 per cent. of the seed. By the aid of a temperature not exceeding 200° F., and powerful and long-continued pressure, as much as 28 per cent. of very good oil can be obtained. The cake forms a valuable cattle food. The Italian variety is said to have a much more highly oleaginous seed than the Russian.

Linseed-oil has a faint colour, and mild odour and flavour when pure, but the commercial article is dark-yellow, with sharp repulsive flavour and odour. Its sp. gr. is 0·930 ; at 0° F., a little solid fat separates out; at - 4° F., it solidifies. By exposure to the air, after heating with oxide of lead, it rapidly dries up to a transparent varnish. The fresh oil saponifies readily, giving a yellow and very soft soap with soda; by saponification, it yields 95 per cent. of fatty acids, chiefly linoleic, with a little oleic, palmitic, and myristic acids. It dissolves in 1·6 parts of ether, and in 32 parts of alcohol at 0·820 sp. gr. The oil is very extensively used in the manufacture of paint and oil-varnishes. For artists' use it is purified by shaking up with whiting, and warming. Linseed-oil is never met with in commerce really pure, nor even the seed itself. Previous to the Crimean War, it was a recognised custom at the Black Sea ports to add one measure of hemp or other seed to every 39 of linseed. Since then the proportion has advanced to 1 in 19, in addition to which the Indian seed is grown mostly as a mixed crop with

mustard and colza : pure linseed oil can only be obtained by picking out the seeds individually.

Linseed-oil, to be suitable for painting, must dry well. A reliable test is to cover a piece of glass with a film of the raw oil, and to expose it to a temperature of about 100° F. The time which the film requires to solidify is a measure of the quality of the oil. If the oil has been extracted from unripe or impure seed, the surface of the test-glass will remain "tacky" or sticky for some time, and the same will happen if the oil under examination has been adulterated with either an animal or vegetable non-drying oil.

Until recently, linseed oil was frequently adulterated with cotton-seed oil, extracted from the waste seeds of the cotton plant. Where the admixture was considerable, it could easily be detected by the sharp, acrid taste of the cotton-seed oil. Now, however, means have been found for removing this disagreeable taste, and the consequence has been that cotton-seed oil is so largely used for adulterating olive-oil, or as a substitute for it, that its price has risen above that of linseed oil.

Another adulterant which is rather difficult to detect is rosin. Oil containing this substance is thick, and darker in colour than pure oil. When the proportion of rosin is considerable, its presence may be ascertained by heating a film of the oil upon a metallic plate, when the characteristic smell of burning rosin will be perceptible. When the percentage of rosin is too small for detection in this manner, a film of the oil should be spread upon glass and allowed to dry. When quite hard, the film should be scraped off, and treated with cold turpentine, which will dissolve any rosin which may be present, without materially affecting the oxidised oil. The presence of rosin may also be detected by the following simple chemical test. The oil is boiled for a few minutes with a small quantity of alcohol (sp. gr. 0·9), and is allowed to stand until the alcohol becomes clear. The supernatant liquid is then poured off, and treated with

an alcoholic solution of acetate of lead. If the oil be pure, there will be but a very slight turbidity, while the presence of rosin causes a dense flocculent precipitate. Should linseed oil be adulterated with a non-drying oil, it will remain sticky for months when spread out in a thin film upon glass or any other non-absorbent substance.

The sp. gr. of linseed oil is, in some cases, of value in estimating its quality; but as the variations are slight, it would be difficult to detect them in so thick a liquid by means of an ordinary hydrometer. A simple method of obtaining an approximate result is to procure a sample of oil of known good quality, and to colour it with an aniline dye. A drop of this tinted oil will, when placed in the oil to be tested, indicate, by its sinking or swimming, the relative density of the liquid under examination. Freshly-extracted linseed oil is unfit for making paint. It contains water and organic impurities, respecting the composition of which little is known, and which are generally termed "mucilage." By storing the oil in tanks for a long time, the water and the greater part of the impurities are precipitated, forming at the bottom of the cistern a pasty mass known as "foots."

To accelerate the purification of the oil, and to remove at least a portion of the colouring matter, various methods are in use. The action of sulphuric acid upon linseed-oil is not so favourable as upon other oils. It is, however, sometimes employed, in the proportion of two parts of a mixture of equal volumes of commercial sulphuric acid and water to 100 parts of oil. The dilute acid is poured gradually into the oil, and the mixture is violently agitated for several hours. It is then run into tanks, and allowed to settle. A concentrated solution of chloride of zinc has been substituted for sulphuric acid in the proportion of about  $1\frac{1}{2}$  per cent. of the weight of the oil. When the reaction is complete, steam or warm water is admitted into the liquid, in order to clarify it. Oil treated in this way loses a considerable proportion of the colouring matter which it originally contained.

When the oil is to be used for white paint, it is sometimes bleached by exposing it to the action of light. On a large scale, this is done by placing it in shallow troughs, lined with lead and covered with glass. The lead itself appears to have some influence upon the bleaching of the oil, for the decoloration is not so rapid if the troughs be lined with zinc. For small quantities, a shallow tray of white porcelain or earthenware, similar to those in use for photographic purposes, gives very good results, the white surface increasing the photo-chemical action. It is not quite clear whether the presence of water accelerates the bleaching of oil by this method; some manufacturers consider its presence necessary, others omit it. Various salts are added to the water, the one most in use being copperas.

However the oil may have been prepared, it will, if kept a long time, deposit a sediment. At first this contains mucilage; but the sediment from old oil consists chiefly of the products of decomposition of the oil itself. The presence of oxygen is not necessary for this decomposition; but it is increased by the action of light. Raw linseed-oil dries more slowly than boiled; but the resulting film is more brilliant and durable. Raw and boiled oil are therefore usually mixed in proportions varying according to the time which can be allowed for the paint to dry, or to the properties required of the film. For the ordinary kinds of paint, equal parts of boiled and raw oils are customary. Linseed-oil heated to a temperature of 350°–400° F. dries much more rapidly than in its raw state.

MENHADEN OIL.—A fish eagerly sought for its oil on the Atlantic coast of America, is the "Menhaden" or "porgie" (*Alosa [Brevoordia] Menhaden*), a member of the herring family, about 8–14 in. long. The fishery is carried on all along the coast from Maine to Maryland. The fish leave the Gulf Stream and strike the coast of New Jersey in April, reaching the coast of Maine in May–June, and remaining till October–November. They migrate in enormous schools, and

are caught in seines, carried by the fastest and smartest yachts. Very few of the fish are sent to the table; nearly all are boiled down for their oil.

This is performed in the following manner:—The fish are shot into receiving-tanks situated outside the building; thence a sliding door opens into the boiling-tanks, which are long, watertight, uncovered boxes, of varying capacity, provided with a coil of perforated pipe for the admission of steam, and a plug-hole for the exit of the liquid after boiling. Some water is put into the tanks ready for the fish, and as soon as the latter have been introduced, steam is turned on, and the whole mass is boiled for 20–40 minutes. When the cooking is completed, the liquor, containing a portion of the oil of the fish, is drawn off into settling tanks, for the recovery of the oil. The “pomace” or cooked fish is raked into “curbs,” perforated cylinders fitted with hinged bottoms, and these, when full, are placed under hydraulic presses. Pressure is applied so long as water and oil continue to escape from the mass. The remaining solid matters, called “scrap,” are treated for the preparation of a fertilising compost. The oil and water pass by gutters into settling tanks, where the oil soon rises to the surface, and is skimmed off, or allowed to escape over a separating partition.

The oil is still crude, and requires clarifying and bleaching before it becomes a saleable commodity. This is effected in several ways. It is first boiled, to free it completely from water. It is purified from solid matters by running it into filter-bags suspended over casks, and then subjecting it to pressure in bags, the oil escaping while the sediment remains in the bags. This refuse, termed “foots,” is bleached and used for soap-making. The oil thus refined is termed “straits,” and is ready for barrelling. “Bank” is an inferior grade. Bleaching is sometimes performed by exposure to the sun in shallow tanks, having glass covers to exclude dust when a superior quality is desired.

Its principal application in America is for tanning and

currying purposes. In France, it is largely employed as a substitute for cod-liver oil. In this country, it is often passed off as olive-oil, and considerable quantities of it are mixed with linseed-oil for painters' use. The rapidity with which it oxidises, and its good body, render it not unsuitable as a vehicle for paint.

POPPY-SEED OILS.—Oil is yielded by the seeds of three kinds of poppy—the opium-poppy (*Papaver somniferum*), the spiny-poppy (*Argemone mexicana*), and the yellow-horn poppy (*Glaucium luteum*).

In Asia Minor and Persia, after the collection of the opium from the poppy-heads, the latter are gathered, and the seed is shaken out and preserved. It is black, brown, yellow, or white; some districts produce more white seed than others. The seed is pressed in wooden lever presses to extract the oil, which is used by the peasants for culinary and illuminating purposes. Some of the seed is also sold to Smyrna merchants, who ship it to Marseilles, where it is employed in soap-making, and as a substitute for linseed-oil. The average yield of oil is 35–42 per cent., the white seed being considered the richest.

The same economy takes place in India, where the plant is also grown for the sake of its seed alone in some districts. In this latter case, the sowing takes place in March–April, about 2 lb. of seed being sown broadcast to one acre. The seed vessels ripen in August; the heads are then cut off, sun-dried, sorted, and trodden out in bags, or threshed. The seed is immediately crushed and pressed, the yield of oil being in proportion to the freshness of the seed, and amounting to 14 oz. from 4 lb. under favourable conditions. The oil readily bleaches by exposure to the sun in shallow vessels, and is then transparent and almost tasteless. The natives use it very largely for cooking purposes, and as a lamp-oil. The cake is consumed as food by the poorer classes. The unpressed seed is largely exported from India.

France grows a large quantity of poppy-seed at home, over

100,000 acres having been returned as under this crop some few years since. The French oil is of two kinds, a white cold-drawn oil, and a coarser oil obtained by a second expression and from inferior seed, the total yield being 40 per cent. The finer oil is fit for alimentary purposes, and is largely used to adulterate olive-oil; it is also employed as a lamp-oil, and very extensively by artists for grinding light pigments, as, though possessing less strength and tenacity than linseed-oil, it keeps its colour better. The pure oil has a golden-yellow tint and agreeable flavour; its sp. gr. is 0·924 at 59° F.; it solidifies at 0° F., and remains long in this state at 28½° F., is slow to become rancid, and saponifies readily; dissolves in 25 parts cold and 6 parts boiling alcohol, and dries in the air more rapidly than linseed oil.

*Glaucium luteum* is a common plant on the sandy shores of the Mediterranean, the western coast of Europe as far as Scandinavia, and some parts of North America. It is very hardy and cultivated with little trouble. It prefers stony and chalky soils, where few other plants will thrive, and has therefore been recommended for culture on such otherwise waste land. Under cultivation, it affords about 10 bush. of seed per acre. The seed contains 42½ per cent. of oil, and yields about 32 per cent. by pressure. The oil obtained by cold expression is devoid of odour and flavour, and has a sp. gr. of 0·913. It is applicable to culinary and illuminating purposes, as well as for soap-making and paint. The cake is a good phosphatic manure. It seems to have been very little utilised, probably on account of the comparatively small yield of seed.

TOBACCO-SEED OIL.—The seeds of the tobacco-plant contain about 30 per cent. of a fatty oil, which is extracted by powdering them, kneading them into a stiff paste with hot water, and pressing hot. The oil is clear, limpid, golden-yellow in colour, inodorous, and mild flavoured; its density is 0·923 at 59° F.; it remains liquid at 6° F., dissolves in 168 parts of alcohol at 0·811 sp. gr., and saponifies readily. One

authority excludes it from the drying oils ; another considers its drying quality to be unusually developed, and recommends it for paints and varnishes.

WALNUT OIL.—The common walnut (*Juglans regia*) is found native from Greece and Asia Minor, over Lebanon and Persia, along the Indu Kush to the Himalayas, and from the Caucasus almost throughout China, besides having been introduced generally throughout temperate Europe. In portions of the Alps and Apennines, it is very abundant, and is fairly plentiful in the forests of Lazistan, on the Black Sea, but is perhaps most common in Cashmere, whence come the walnuts imported into the plains of India.

The albuminous kernel of the walnut affords some 50 per cent. of oil. It is said that it furnishes one-third of all the oil made in France ; it is extensively prepared in the central and southern departments, notably Charente, Charente-Inférieure, and Dordogne, where it is commonly met with in barrels of 50 *kilo*. In both Spain and Italy, outside the olive-region, walnut-oil is largely expressed. It is of considerable importance in the hill districts of India, but is seldom seen in the plains. Cashmere and Circassia also include it among their industrial products.

The oil should not be extracted from the nuts until 2–3 months after they have been gathered. This delay is absolutely necessary to secure an abundant yield, as the fresh kernel contains only a sort of emulsive milk, and the oil continues to form after the harvest has taken place ; if too long a period elapse, the oil will be less sweet, and perhaps even rancid. The kernels are carefully freed from shell and skin, and crushed into a paste, which is put into bags and submitted to a press ; the first oil which escapes is termed “virgin,” and is reserved for feeding purposes. The cake is then rubbed down in boiling water, and pressed anew ; the second oil, called “fire-drawn,” is applied to industrial uses. The exhausted cake forms good cattle-food.

The virgin oil, recently extracted, is fluid, almost colour-

less, with a feeble odour, and not disagreeable flavour. Its sp. gr. is 0·926 at 59° F., and 0·871 at 201° F.; it thickens to a butter-like consistence at 5° F., and solidifies to a white mass at -17½° F. In the fresh state, it is largely used in Nassau, Switzerland, and other countries, as a substitute for olive-oil in salads, &c., but is scarcely to be considered as a first-class alimentary oil. The fire-drawn oil is greenish, caustic, and siccative, surpassing linseed-oil in the last respect, and exhibiting the property more strongly as it becomes more rancid. On this account it is preferred by many artists before all other oils.

WOOD-OIL OR TUNG-OIL.—This fatty oil is a product of the so-called “oil tree” of China, Cochin China, and Japan (*Aleurites cordata* [*Elaeococca vernicia*, *Dryandra cordata*]), and must not be confounded with the Malayan article, which is an oleo-resin. The fruit capsules of the *tung* are filled with rich oil-yielding kernels, from which 35 per cent. by weight of oil may be obtained by simple pressure in the cold. The sp. gr. of the oil is 0·9362 at 59° F. It possesses several remarkable properties: heated to 212°–392° F. out of contact with the air, it retains its original limpidity after cooling, but in contact with the air it solidifies almost instantaneously, melting again at 93° F., and exhibiting the same elementary composition; the cold expressed oil rapidly solidifies by light in the absence of air; and its drying qualities exceed those of any other known oil. It is devoid of colour, odour, and flavour. The oil is produced in immense quantities in China; in the provinces of Ichang and Szechuen, it is one of the principal articles of native manufacture.

In China the oil is universally employed for caulking and painting junks and boats, and for varnishing and preserving woodwork of all kinds. The oil is unknown to European commerce, but an attempt to naturalise the tree in Algeria has been projected. Its industrial value has been too long neglected.

EXTRACTION OF SEED-OILS.—The old-fashioned crude appa-

ratus for extracting oil from seeds, which answered the purposes of our forefathers, has had to give way to modern improved machinery, such as that manufactured by Rose, Downs & Thompson, of Hull, and shown in the subjoined illustrations.

The arrangement of the mill is shown in plan in Fig. 33 and in elevation in Fig. 34. The seed or other material

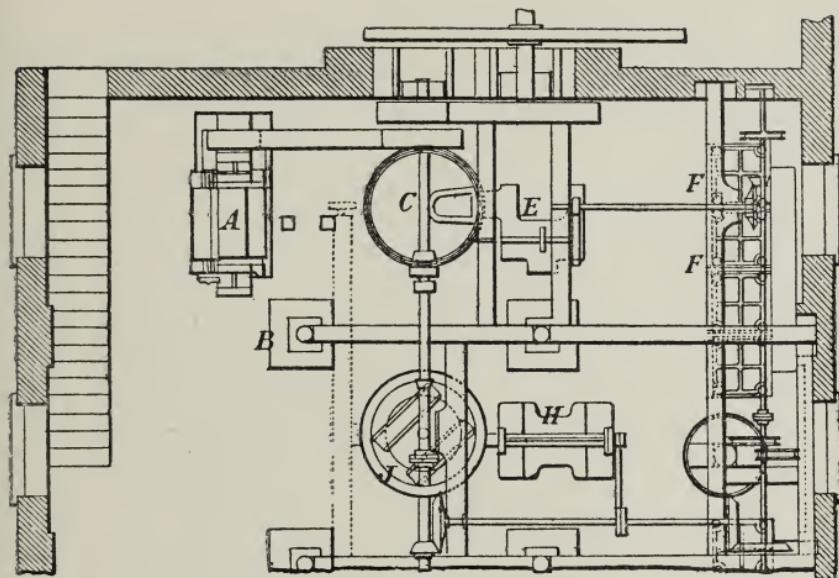


Fig. 33.—SEED-OIL MILL.

passes through the following course:—It runs from an upper floor through the roll frame A, by which it is crushed three or four times; it is then taken by the elevators B to the kettle C, where it is heated and damped. From beneath the kettle, it is drawn, in quantities sufficient to make a cake, by a box which conveys it to the moulding machine E. Here it undergoes preliminary compression, the objects of which are (1) to increase the number of cakes which may be inserted in the presses at one time, enabling 18 12-lb. cakes to be made where 4 8-lb. cakes were formerly made, and (2) to

ensure uniform size and weight, and uniform density or consistence throughout.

The cakes are removed from the moulding machine, and put into the press F, 3 or 4 of which are required to each moulding machine. The pressure is applied either by means of hydraulic pumps, or by a high and low pressure accumu-

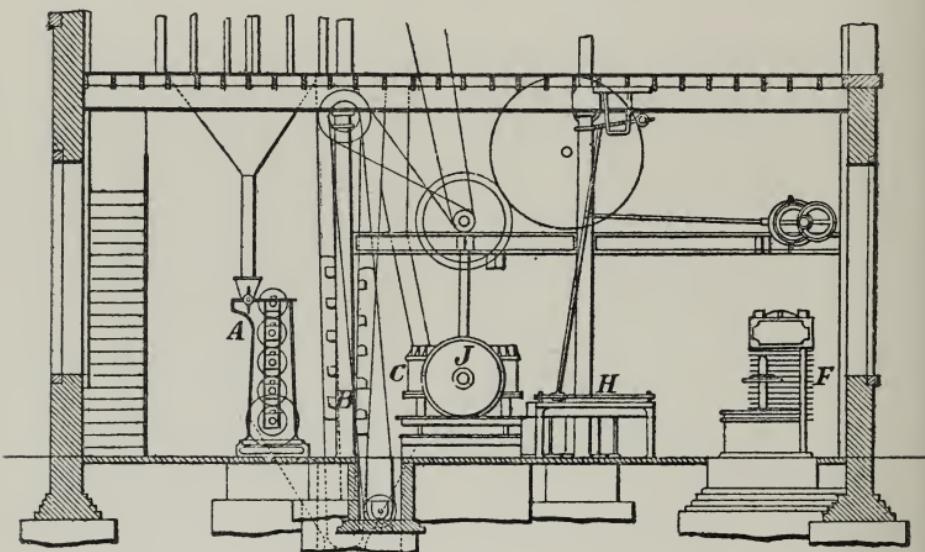


Fig. 34.—SEED-OIL MILL.

lator; but unless extreme care is used with the latter, it gives too rapid a pressure, squirting out the seed at the side of the plates, and exercising a destructive effect upon the cloth employed. The pulsation caused by the pumps working directly to the press cylinder is more akin to the action of a wedge, and seems to extract the oil better than the dead pressure given by the accumulator. If the latter is used, a small cylinder may be applied to give the preliminary pressure in the moulding machine, in lieu of a cam. After remaining under pressure about 25 minutes, the cakes are withdrawn, and after being stripped of the cloth, are pared by the machine H, which completes the manufacture of the

cakes. The parings fall under a very small pair of edge-running stones J, which automatically discharge them when sufficiently ground, into an elevator conducting to the kettle, where they are worked up with fresh seed. In a mill with 4 presses, 2 men and a boy in the press room can make 6 tons of cake in 11 hours, a rate of production requiring 6 men by

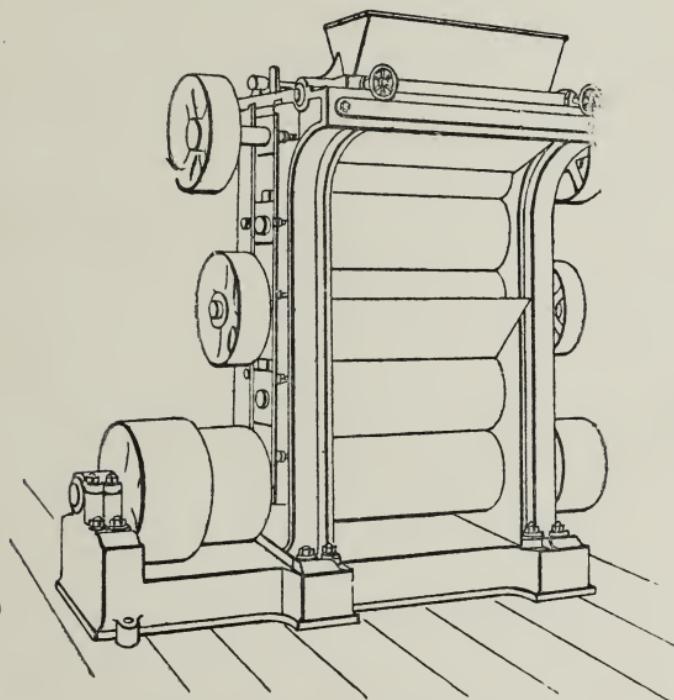


Fig. 35.—SEED-CRUSHING ROLLS.

the old process. The saving in steam power is about 30 per cent., chiefly due to the absence of the heavy edge runners, which also effects an economy of space. About 2 per cent. more oil is extracted, and the cakes are improved in appearance by not having the structureless texture caused by the trituration of the seed under edge-runners.

Having described the general routine of the process, some details may be added concerning the working of the several machines. The roll-frame, Fig. 35, consists of 4 or 5 chilled-

iron rolls, each 3 ft. 6 in. long by 16 in. in diameter, placed one above the other. These rolls are used for crushing all the seed that passes through one set of presses, making  $5\frac{1}{2}$ - $6\frac{1}{4}$  tons linseed-cake per spell of 11 hours. The seed passes into the hopper in the usual manner, and is distributed to the crushing-rolls by a fluted feed roll the same length as the crushing-rolls, placed at the bottom of the hopper. When the seed passes the feed roll, it falls on a guide-plate that carries it between the 1st and 2nd roll. After passing between these rolls and being partly crushed, it falls on a guide-plate on the other side, which carries it back between the 2nd and 3rd rolls, where it is crushed more fully. It then falls on another guide-plate, which carries it between the 3rd and 4th rolls, where it is ground more fully. Then it falls on a 4th guide-plate, and is conveyed between the 4th and 5th rolls to receive the finishing touch. It is thus crushed four times.

The kettle is shown in Fig. 36, which represents one capable of heating sufficient seed to keep four 16-plate presses occupied, or to make 6 tons of cake per 11 hours. It is steam jacketed and furnished inside with a damping apparatus. The inside diameter is 5 ft., and the depth 2 ft. 6 in. The seed introduced is kept in motion by the stirring gear, and when sufficiently heated and damped, is withdrawn by the box A in quantities to form one cake, and transferred at once to the moulding machine, attached or separate.

This machine is illustrated in Figs. 37, 38. Its purpose is to measure the quantity of seed required to make each cake, to shape it as required, and to press it so much, without extracting any oil, as will enable the greatest number of cakes to be put into the press. The measure of seed is placed on a strip of woollen cloth, spread upon a thin iron tray, sliding on the guides B; the bottomless hinged mould C, having the exact shape of the intended cake, is closed upon it, and the measure A (Fig. 36), which is also bottomless, is drawn over guides in the upper surface of the mould C, thus ac-

curately distributing the seed. The mould is next thrown upon its hinge (Fig. 37), and the ends of the strip of cloth are folded over the seed, the thickness of which is about  $3\frac{1}{2}$  in. The thin iron tray, with the mould of seed upon it, is

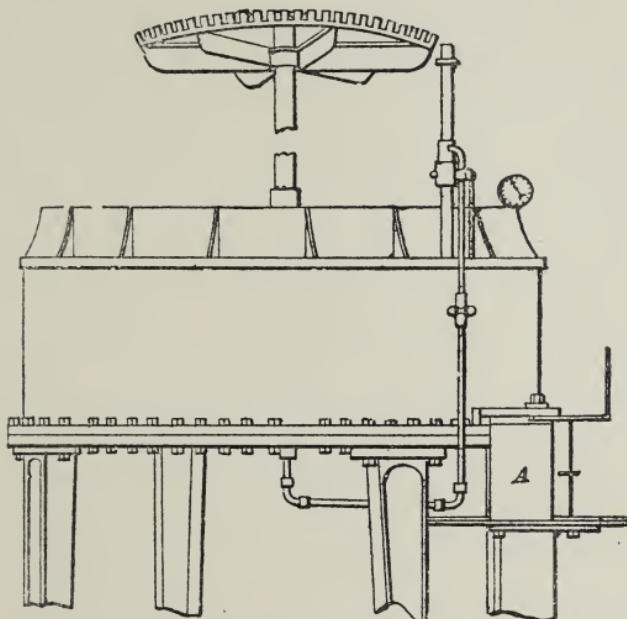


Fig. 36.—SEED-BOILING KETTLE.

then pushed along the guides B, beneath the die D. This action gives motion to a cam, shown above in the illustrations, but which may be placed beneath if necessary. This cam brings down the die and compresses the mould of seed to a thickness of  $1\frac{1}{4}$  in.; its revolutions are so timed that the seed is under pressure long enough (about one-third of a minute) to let the workman have another cake ready.

When the die of the moulding-machine rises, the cake and tray are removed and placed in the press (Fig. 39), the tray being withdrawn. The plates of the press are slightly thickened towards the edges, and bear the name of the

manufacturer in reverse. The press is suitable for extracting oil from linseed, rape-seed, cotton-seed, hemp-seed, niger-

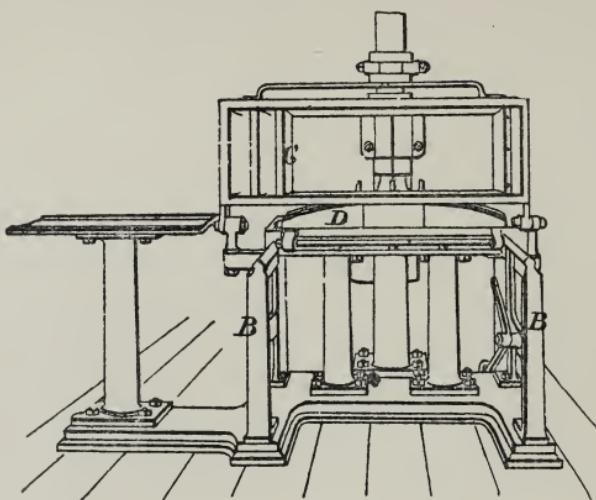


Fig. 37.—OIL-CAKE MOULDING MACHINE.

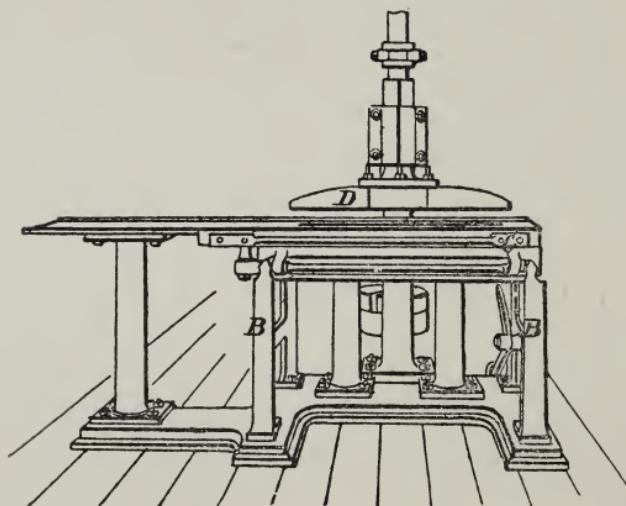


Fig. 38.—OIL-CAKE MOULDING MACHINE.

seed, sunflower-seed, gingelly-seed, castor-seed, ground-nuts, coco-nuts, olives, &c. It is made in various sizes. The No. 1

double press (not shown) is furnished with 4 cake boxes, suitable for making 4 tapered cakes at one pressing, each about 2 ft. 5 in. long, by  $10\frac{1}{2}$  in. wide at one end, and  $7\frac{1}{2}$  in. at the other, when using linseed, 48 lb. of Bombay seed being required to charge the press, and giving a cake weighing

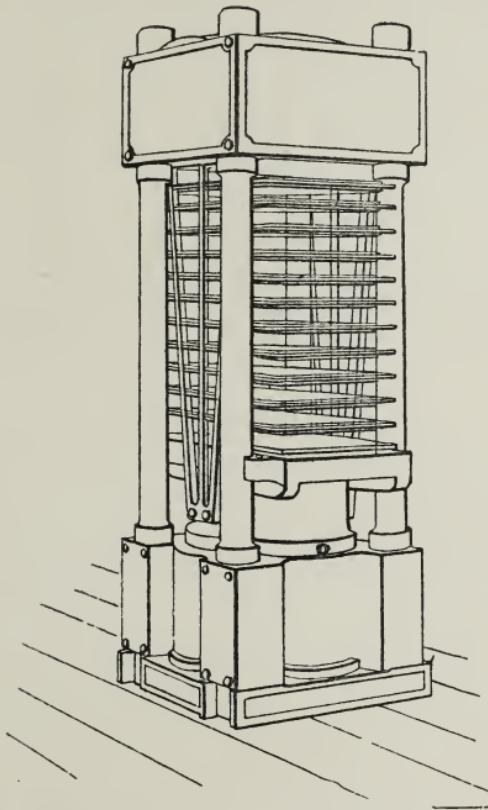


Fig. 39.—OIL-SEED PRESS.

about 8 lb.; the maximum and minimum weights of its charges are 60 lb. and 40 lb., of the cakes, 13 lb. and  $6\frac{1}{2}$  lb. The charges vary from 3 to 6 an hour, being 4 for cotton-seed and 5 for linseed; most other seeds are worked the same as linseed, but rape and gingelly are worked twice. By using 2 presses for the first time and 3 for the second, 3 presses will crush as much seed as 5. These presses are made of a capacity to take 270-320 lb. of seed at a

charge, giving cakes of 9-15 lb., and requiring 30-45 minutes for the operation. In all these presses, the hair wrappers, weighing some 26 lb., used in the old process, are dispensed with.

A very complete account of oils and fats will be found in Spon's 'Encyclopaedia of the Industrial Arts,' to which the reader is referred for further information.

**DRYERS.**—The maximum of drying power in oils is obtained by the addition of certain metallic oxides, which not only part with some of their own oxygen to the oil, but also act as carriers between the atmospheric oxygen and the heated liquid. This heating of the oil with oxides is known as boiling, although the liquid is not volatilised without decomposition, as is the case with water. At about 500° F., bubbles begin to rise in the oil, producing acrid, white fumes on coming into contact with the air. The gas thus given off consists chiefly of vapour of acrolein mingled with carbonic oxide. There is no advantage in heating the oil to a higher temperature than 350° F. Accurate experiments have shown that the drying properties of the oil are not increased by heating it beyond this point, while its colour is considerably darkened.

For the finer qualities of boiled oils, it is essential that the raw oil should have been stored for some time, so that it may be free from mucilage. This mucilage is the chief source of the dark colour of some boiled oils; when heated, it forms a brown substance, which is soluble in the oil itself, and extremely difficult to remove.

The oxides usually added to the oil during boiling are litharge or red-lead, the former being preferred on account of its lower price. About 2-5 per cent. by weight of the oxides or dryers is gradually stirred into the oil after it has been slowly raised to a temperature of about 300° F. The stirring should be continued until the litharge is dissolved, or it would cake on the bottom of the pan, and cause the oil to burn. Litharge may even be reduced to a

cake of metallic lead when the fire is brisk. Some pans are furnished with stirrers and gearing by which the latter can be worked, either by hand or steam. The material of which the pans are made is either wrought or cast iron. Copper pans are sometimes used with the object of improving the colour of the oil.

Little is known respecting the chemical reactions which take place during the boiling of oil. Even when the air is excluded during the process, the drying properties are greatly increased, and, if boiled long enough, the oil is converted into a solid substance. The loss of weight which ensues is dependent upon the temperature and the time during which the operation continues. It is less when the air is freely admitted than if the pan is covered with a hood. The vapours given off by the oil are of an extremely irritating character, and should be destroyed by passing them through a furnace. As their mixture with air in certain proportions is explosive, this furnace should be situated at some distance, and the gases be conducted into it by means of an earthenware pipe.

Since zinc oxide has been introduced as a substitute for white lead in painting, researches have been made to replace litharge as a dryer, because it is not logical to discard the lead pigment and then use a lead dryer with a zinc pigment.

Several metallic oxides and salts, especially zinc sulphate, manganese oxide, and umber, have the property of combining with oils, which they render drying. To these may be added the protoxides of the metals of the third class, i. e. iron, cobalt, and tin. But these oxides are very unstable and difficult of preparation; hence it became desirable to discover some means by which they might be combined with bodies which would enable them to be prepared cheaply, and at the same time leave unimpaired their desiccating powers. Moreover, it is acknowledged that dryers in the dry state are preferable in many respects to drying oils. Following are some of the recently introduced dryers:—

*Cobalt and Manganese Benzoates.*—Benzoic acid is dissolved in boiling water, the liquid being continually stirred, and neutralised with cobalt carbonate until effervescence ceases. Excess of carbonate is removed by filtration, and the liquor is evaporated to dryness. The salt thus prepared is an amorphous, hard, brownish material, which may be powdered like rosin, and kept in the pulverulent state in any climate, simply folded in paper. Painting executed with a paint composed of 3 parts of this dryer with 1000 of oil and 1200 of zinc-white, dries in 18 to 20 hours. Manganese benzoate is prepared in the same way, substituting manganese carbonate for that of cobalt. Applied under similar circumstances, it dries a little more rapidly, and a little less is required. Urobenzoic (hippuric) acid is equally efficacious.

*Cobalt and Manganese Borates.*—These salts also, in the same proportions, are found to be of equal efficacy. The latter is extremely active, and requires to be used in much smaller proportions.

*Resinates.*—If an alkaline resinate of potash or soda be dissolved in hot water, and this solution be precipitated by a solution of a proportionate quantity of a cobalt or manganese chloride or sulphate, an amorphous resinate is formed, which, after being collected on cloth filters, washed, and dried, forms an excellent drier.

*Zumatic (Transparent) Dryer.*—Take zinc carbonate, 90 lb. ; manganese borate, 10 lb. ; linseed - oil, 90 lb. Grind thoroughly, and keep in bladders or tin tubes ; the latter are preferable.

*Zumatic (Opaque) Dryer.*—Manganese borate, as a dryer, is so energetic that it is proper to reduce its action in the following way :—Take zinc-white, 25 lb. ; manganese borate, 1 lb. Mix thoroughly, first by hand, then in a revolving drum ; 1 lb. of this mixed with 20 lb. paint ensures rapid drying.

*Manganese Oxide.*—Purified linseed-oil is boiled for 6 or 8

hours, and to every 100 lb. boiled oil are added 5 lb. of powdered manganese peroxide, which may be kept suspended in a bag, like litharge. The liquid is boiled and stirred for 5 or 6 hours more, and then cooled and filtered. This drying oil is employed in the proportion of 5 to 10 per cent. of the zinc white.

*Guynemer's.*—Take pure manganese sulphate, 1 part; manganese acetate, 1 part; calcined zinc sulphate, 1 part; white zinc oxide, 97 parts. Grind the sulphates and acetate to impalpable powder, sift through a metallic sieve. Dust 3 parts of this powder over 97 of zinc oxide, spread out over a slab or board, thoroughly mix, and grind. The resulting white powder, mixed in the proportion of  $\frac{1}{2}$  or 1 per cent. with zinc-white, will enormously increase the drying property of this body, which will become dry in 10 or 12 hours.

*Manganese Oxalate.*—A writer in the *Moniteur de Produits Chimiques* draws attention to the properties possessed by manganese oxalate as a drier. This salt has hitherto not had any important industrial uses, but it can be readily prepared in a state of purity from the native carbonate by the action of oxalic acid; the author is of the opinion that it will be found of use for this purpose. If prepared from carbonate free from iron and lime, it can be obtained as a fine crystalline white powder, and two-fifths per cent. suffices to bring about the change. The oxalate is resolved by heat into manganese oxide, carbonic acid and carbon monoxide, and in the presence of fatty acids the manganese oxide formed combines with them, the decomposition taking place at about  $130^{\circ}$ . The operation is carried out by mixing in a mortar the oxalate with two or three times its weight of oil, and then adding the mixture to the main portion of the oil. The heat should be applied gradually, and the decomposition is known to be complete when there is no further evolution of gas. The boiled oil, under this treatment, preserves its limpidity and also remains colourless. Manganese oxalate

has the advantage over oxide of lead, which is commonly employed for this purpose, in causing the oil to remain transparent when exposed to sulphur vapours. Manganese acetate has also been used, but it likewise causes a darkening in the colour of the oil, and the nitrate is dangerous owing to the possible action of nitric acid on the fats present in the oil. Manganese borate appears to be next in value to the oxalate as an oil drier.

In a paper recently read before the Society of Arts, Prof. Hartley remarked that paint, such as is used for ordinary purposes, is essentially composed of three materials, without taking into account the coloured pigments.

(1) White lead, or sublimed zinc-white.

(2) An oil, generally linseed or poppy oil, which is ground up with the white lead or zinc-white until it becomes a soft paste. This is mixed with variable preparations of linseed oil and spirit of turpentine.

(3) A substance called dryers, or siccative materials; it may be linseed oil in which litharge is dissolved, or it may be linseed oil containing a compound of manganese.

Paint owes to the dryers its property of drying more rapidly than it would do without it; and it is considered indispensable in buildings in all cases where paint applied to wood, stone, or metal, would not be quite dry in 48 hours, or at most in 72 hours, after the first application.

The first question which requires an answer is, what chemical process takes place when a paint dries.

BOILED OIL.—Linseed oil absorbs oxygen; and, when the oil contains manganese, it absorbs oxygen much more greedily; and when a manganese oil—that is to say, a boiled oil containing manganese—is mixed with linseed oil, the substance absorbs oxygen, from a limited supply of air contained in a closed space, until no trace of any other gas but nitrogen remains. The power of absorbing oxygen possessed by 100 volumes of linseed oil, compared with that of 100 volumes of a mixture of linseed oil and so-called man-

ganese oil, is as 9·4 to 100. This may be termed the measure of its drying power. A mixture of linseed oil, with a little more than one-fourth of its volume of manganese oil, has a power of absorbing oxygen four and a half times greater than either of the components of the mixture taken separately. In this case Chevreul argues that linseed oil may be considered as a "dryer" to manganese oil.

Linseed oil, without any addition whatever, if boiled for three hours, becomes a better drying oil than it was previous to the action of heat.

Oil boiled with 10 per cent. of litharge for three hours, is a much better dryer than when heated without this oxide.

Oil boiled alone for five hours is an inferior drying oil to one heated for only three hours.

Oil previously boiled alone for five hours, and boiled alone again for three hours, is scarcely altered in drying power, but it becomes a better drying oil if it is boiled the second time with litharge. It is inferior to a drying oil which has been boiled only three hours with litharge, without being submitted to a previous boiling.

Oil boiled alone for five hours, boiled for a further period of three hours with manganese dioxide which has already been used for one operation, is very nearly as strong a dryer as that which has been boiled with litharge under the same conditions; but it is superior to an oil which has been boiled with manganese dioxide for eight hours. This no doubt arises from the longer boiling with manganese having caused a larger quantity of manganese to dissolve, and that the quantity dissolved is in excess of that which yields the best result.

Finally, oil boiled for five hours, and then boiled alone once more for eight hours, becomes viscous, and the first coat requires a considerable time to dry. We thus see that the oxides of lead and of manganese in certain proportions concur with heat in increasing the drying power of linseed oil. This drying of oils is a process of slow oxidation.

The following points of Chevreul's appeared to be difficult of satisfactory explanation, and suggested to Prof. Hartley an examination *de novo* of the facts, as well as an investigation of the chemistry of the subject generally:—

1. Linseed oil not boiled acted as a dryer to the same oil boiled with manganese dioxide.

2. Linseed oil, boiled with either litharge or manganese dried more rapidly when mixed with turpentine.

3. Oil, mixed with white lead, zinc white, antimony white, and arseniate of tin, acts differently, thus:—The white lead dries most rapidly, the zinc white next, but antimony white and arseniate of tin are incapable of acting as dryers, in fact, they retard the drying process.

4. Oil boiled alone for five hours, and boiled for a further period of three hours with manganese dioxide becomes a superior drying oil to one which has been boiled with manganese dioxide for eight hours.

From a series of experiments, which were continued for two years, on twenty-five weighed quantities of raw linseed oil, Prof. Hartley draws the following deductions:—

1. The chemical action of a manganese compound, when dissolved in linseed oil, is that of a carrier of oxygen from the atmosphere to the oil. Manganese oxide takes up oxygen from the air, and transfers it to the oil, and in so doing it suffers alternately the opposite processes of oxidation and reduction.

2. To obtain the best result, the amount of manganese present must not exceed a certain small proportion of the oil.

3. Oil to which turpentine has been added dries more rapidly than oil without such addition, because the oil being diluted and rendered thinner, it spreads over a larger surface, and is in contact, therefore, with a much larger quantity of oxygen.

4. Turpentine does not act as a dryer, that is, as a carrier of oxygen to linseed oil.

5. Different white pigments behave differently when

drying, because the more powerfully basic the properties of the pigment, the more powerful is its action as a dryer. Lead oxide and white lead (basic lead carbonate) combine more easily with the acids of linseed oil than zinc oxide does. But zinc oxide dries better than antimony oxide, because it is a stronger base, while arseniate of tin has no basic properties, therefore does not act as a dryer.

Different substances, that is to say, those without chemical action on oil, such as lamp-black, sulphate of baryta, and sulphate of lead, cannot act as "dryers."

Linseed oil is a glyceride of a peculiar acid, called linoleic acid. Whatever the exact constitution of linoleic acid may be, linseed oil for the most part is composed of trilinolein. Raw linseed oil contains the following constituents:—

1. Glyceride of linoleic acid or trilinolein  $\left\{ \begin{array}{c} \text{C}_{18}\text{H}_{31}\text{O} \\ \text{C}_3\text{H}_5 \end{array} \right\} \text{O}_3$ .

2. Water.

3. Mucilage, with the composition  $n(\text{C}_6\text{H}_{10}\text{O}_5)$ . On boiling with dilute acids this yields a gum and a sugar.

4. An essential oil, present in minute proportions, and of unknown composition.

5. A mixture of colouring matters of intense tinctorial power, viz. blue and yellow chlorophylls and erythrophyll.

The only useful and desirable substance is the trilinolein.

The effect of oxidation upon linseed oil is to destroy all the glycerine, and to produce therefrom carbonic, formic, and acetic acids, together with some acrolein. When boiled at a high temperature without the addition of any metallic oxide, the glyceride is decomposed, acrolein is formed, and linoleic acid is set free. In fact, whether oil is oxidised by air or by metallic oxides, or whether it be simply heated, the action in each case first leads to the destruction of the glycerine and the liberation of linoleic acid. But linoleic acid very readily absorbs oxygen, and the oxidised substance becomes a tough elastic solid, which is essentially a varnish.

In fact, the process which an oil undergoes in drying is

not desiccation, or depriving it of moisture or of glycerine, but solidification, and the technical term "drying" is a misnomer. That, however, is of little consequence if we really know what is the chemical action of the "drying" process. When oxidised even at a low temperature, the glycerine is destroyed, and the oxidised products form a tough varnish.

There are various methods of converting linseed oil into a drying oil or varnish :—

1. Heating it to a high temperature with litharge.
2. Heating with red oxide of lead.
3. Heating with metallic lead.
4. Heating to a high temperature with manganic oxide.
5. Heating with manganese borate.
6. Heating with manganese oxalate.
7. By the joint action of air and heat upon the oil and manganous oxide, or a solution of manganese dioxide or manganous oxide in the oil.

In the processes 1, 2, 3, there can be no doubt that a lead of linoleic acid is produced, and that this facilitates further oxidation in air, by forming salts with some of the acid products of such oxidation, while the oxidation of the linoleic acid continues. Heating with red lead favours oxidation, by the compound itself conveying oxygen to the oil. In the case of metallic lead, it must be noted that the metal is dissolved. Under certain circumstances, metals become dryers to oils ; thus sheets of metallic lead are capable of acting as dryers to linseed oil.

Linseed oil is pre-eminent in its capacity for absorbing oxygen. This action of metallic lead as a dryer is due to the metal becoming oxidised at the expense of the glycerine of the oil, and so passing into solution by combining with the linoleic acid, or with acetic or formic acid, caused by the oxidation of the glycerine. It is the destruction of the glycerine with concurrent oxidation of the fatty acid which causes the drying or hardening of the oil.

When a drying oil which has been treated with metallic lead, or with litharge, is shaken up with a solution of zinc sulphate, all the lead is precipitated from the oil, and zinc passes into solution therein. By manganese sulphate or copper sulphate, the lead is removed by manganese or copper. Oil charged with lead dries in 24 hours when spread out in a thin layer on glass; it will dry completely in 5 or 6 hours if charged with manganese, in 30 or 36 hours with copper, zinc, or cobalt; and it requires more than 48 hours with nickel, iron, chromium, &c.

Although solidification of a drying oil charged with manganese takes place in from 5 to 6 hours when spread in thin films, the solidification of thicker films requires a longer time. A temperature of 122° to 140° F. accelerates the oxidation of the drying oils, partly because the oil becomes more fluid, and partly because the oxygen is more active at a higher temperature. Hence, oil which has been mixed with an equal volume of turpentine, or a light hydrocarbon, such as benzene, dries more rapidly than oil without such admixture.

When a boiled oil, prepared with manganese, is dissolved in an equal volume of benzene, and shaken up with air in a bottle, rapid absorption of oxygen occurs, especially about 120° F. If fresh air is repeatedly provided, the oxidation is sufficient to cause the liquid to become thick, and, on distilling off the sapient, a perfectly dry and elastic solid remains.

An oil containing manganese is a very superior drying oil to one which has been prepared with lead. This fact, however, is to be noted, that though a large proportion of manganese in an oil may hasten its drying, yet it is disadvantageous, because it does not form so tough a film. This arises from the film becoming hard upon the surface, and so protecting the oil underneath from absorbing oxygen from the air.

Though the oils containing large quantities of dryers dry,

they afterwards lose weight, and become viscous under the same conditions.

Pure linoleates of lead and of zinc are not dryers ; but if heated until it has turned brown, or begun to blacken, a lead dryer becomes effective, although it contains less of the lead compound.

In this case, some compound of lead is formed by absorption of oxygen, which either itself actually oxidises or causes the oxidation of ordinary linseed oil.

Having treated of the materials used for producing boiled oil, and of their action upon the oil, let us now consider how the operation is brought about.

*Process 1.*—Oil is boiled at a high temperature, that is to say, it is heated until frothing and bubbles of gas escape, when litharge or a manganese compound is added.

*Process 2.*—Oil is boiled at a steam heat, with litharge or a manganese compound, in conjunction with a blast of air.

*Process 1.*—The chemical action in the first process is doubtless one which takes place in three stages. It commences by depriving the oil of water ; in the second stage, it destroys the mucilage, by charring it ; in the third, it destroys, in part, the glycerine, and sets free the fatty acids. After the litharge or manganese compound is added, there is formed in the oil a solution of lead salts of the fatty acids, or a manganese salt of the fatty acids.

The oil then, at the high temperature, loses glycerine by oxidation caused by the air, such oxidation being greatly facilitated by the presence of manganese compounds, which are repeatedly oxidised by the air and reduced by the oil, that is to say, they absorb oxygen and pass it over to the oil with great facility.

It matters little, so long as the ultimate action is oxidation, what salt of manganese or what oxide is used, if it be capable of undergoing processes of an alternate character called oxidations and reductions.

It is, however, certain that some manganese compounds

are more suitable than others, owing to their more or less complete solubility in the oil, and their more readily undergoing the two different processes of oxidation and reduction in presence of air and of oil.

*Process 2.*—The credit of being the first to boil oil without resorting to the dangerous expedient of using an open fire and a high temperature in the manufacture, is due to Vincent. He used manganese compounds, or both manganese salts and litharge. His method of boiling oil for the manufacture of printing inks is, with some modifications in technical details, carried out on a large scale at the present time in the preparation of ordinary boiled oil. The essential parts of the plant are a steam-jacketed close boiler with agitating gear, and a pipe for conducting a current of air into the oil by means of a blowing engine. From the head of the boiler there passes a funnel under the back of the furnace fire, by which the disagreeable products of the chemical action are conducted to a place where they are destroyed. These products, as already mentioned, are volatile fatty acids and acrolein.

Oil boiling, as ordinarily carried out, is conducted by means of litharge along with compounds of manganese; in some processes these are mixed with salts of alumina and zinc. The oil so produced is brown and not clear, but it is clarified by keeping. Many samples of such boiled oil deposit insoluble matter when stored for some time, even although they may have become clear previously. This is not a desirable property. Sometimes rosin is added to hasten its drying.

The defects to be noticed, even in the best samples of boiled oil, are the following:—

1. The oil causes a brownish or yellow colour to be communicated to white lead or zinc white.
2. The oil darkens pigments containing brilliantly coloured metallic sulphides, such as vermillion, cadmium yellow, and ultramarine blue.

3. Delicate colours are darkened by the oil when exposed to ordinary town air, that is to say, air which is not quite pure. This is the case even when the oils themselves may not injure the paints.

The causes of such alterations is, in nine cases out of ten, the use of lead dryers.

1. In the first place, boiled oil which contains litharge or other lead compounds takes a permanent brown colour, which affects the purity of white lead, zinc white, and delicate pale tints.

2. Lead forms, with extreme ease, lead sulphide, which, in very minute proportions, is yellow or brown; in larger quantity its colour is black. The lead sulphide is readily formed by contact with other sulphides, as, for instance, vermillion, cadmium yellow, and ultramarine.

3. Boiled oil, containing lead, is coloured brown by exposure to air, owing to the presence of minute quantities of sulphuretted hydrogen, which causes the formation of lead sulphide.

The remedy is obvious: no oil should be used which has been boiled with dryers containing lead. In other words, oil should be boiled with pure manganese compounds only.

In cases where it is desirable to have information of the presence or absence of lead in a boiled oil, the following test will be found most useful:—A mixture is made of 4 oz. of glycerine with 1 oz. of ammonium sulphide, the liquid being kept in a stoppered bottle. Or glycerine is mixed with an equal volume of water, and saturated with sulphuretted hydrogen. Half an ounce of the oil to be tested is placed in a white basin, with the addition of two or three drops of the glycerine solution. The two liquids are thoroughly incorporated, by stirring with a strip of glass. A brown or black colour, which gradually appears, indicates the presence of lead. A pure manganese oil simply becomes slightly yellow. It is true that, if iron is present, a black colour might appear, but iron is also an undesirable impurity. Should it be

required to ascertain that the coloration is or is not caused by iron, two or three drops of glacial acetic acid may be stirred into the oil, when, if the black colour remains, it is certainly not caused by iron.

Under the old process of oil-boiling at a high temperature, the brown colour of the oil was, to some extent, an indication that the oil had been sufficiently heated—that is to say, properly boiled; but in the modern processes, so largely used, in which oxidation is aided by a blast of air, this coloration is no indication whatever of the excellence of the oil; it may be, in fact, the very reverse.

This fact appears to be unknown, or, at any rate, is not a matter of common knowledge among practical men in this country, who, being uninformed as to the methods of preparing the oils, consider that a brown colour is desirable, if not essential.

When oil-boilers were compelled to adopt some expedient to give a reddish-brown colour to the oil, they added a small amount of litharge, the introduction of which actually spoils the oil, and makes it unsuitable for many purposes to which it is otherwise applicable. Of late years, pale boiled oils have been more largely manufactured for special purposes. It is obvious that, for decorative house painting, in which delicate tints are a leading feature, they may be advantageously employed.

Notwithstanding that some of the brown oils, when mixed with white lead, do not entirely retain the brownish tint, but, to some extent, lose it upon drying, yet they never preserve the whiteness of white lead. It follows, therefore, that a pale colour in the oil, provided it is not the yellow colour of raw oil, is greatly to be preferred. Moreover, when paints are mixed with zinc white, no trace of lead should be contained in the oil, otherwise, one of the valuable properties of zinc white pigments is destroyed, namely, its power to retain its whiteness in the atmosphere of a town, because its colour is not affected by sulphuretted hydrogen.

Very generally, zinc white and white lead paints are not mixed with drying oils, but with refined linseed or bleached oil. This, at any rate, is the practice on the Continent. That is to say, the pigments are mixed with an oil from which the impurities, and the natural yellow and red colouring matter, have been removed, so that the colour of the paint is white. If ordinary oil be used, the paint is more or less yellow. In order to render such paint quick drying, a certain amount of dryers, in a solid or liquid form, is added. These dryers almost invariably contain lead, so that zinc white paint is contaminated by lead in another way, which may not be suspected, or which is overlooked.

Now as to the chemical action of dryers on oils. Raw oil contains water and mucilage; the former can be absorbed by anhydrous zinc salts and by dried alum, and solutions of the salts and the salts themselves are capable of precipitating mucilage from the oil; hence these substances cause the impurities to become insoluble, so that they are carried down as "foots." Heat greatly facilitates this action, particularly by causing the oil to become more fluid; and by the action of the anhydrous salts water is withdrawn from the oil. On the "drying" or oxidation of the oil, they exert no chemical action whatever.

Zinc linoleate and lead linoleate do not act as dryers when simply added to the oil. Though the former is soluble in hot oil it is insoluble in cold oil, and it therefore separates from the oil as it cools. The latter is very soluble in linseed oil, but only adds to its drying power when heated therewith.

In conjunction with a high temperature, lead dissolves in oil at the expense of the glycerine, which is decomposed into acrolein, while lead linoleate is formed.

When litharge is heated with linseed oil, the action is somewhat similar, the substances formed being acrolein, lead linoleate, and linoleic acid.

If we consider the action of red lead on trilinolein, we have not only the formation of these lead linoleates, but an excess

of oxygen available for the oxidation of glycerine to acrolein and acrylic acid, or to acetic and formic acids.

These equations serve to show the effect of lead and lead oxides in what may be termed the initiation of the chemical action upon the oil. Subsequent changes, no doubt, depend upon the conditions which obtain at the time, notably upon the temperature and upon access of air to the oil. It is probable that acid linoleates are formed, and that compounds formed from the polymerisation of linoleic acid result eventually.

Whatever doubt there may be as to the action of lead salts, there can be none whatever as to that of manganese compounds. In the first place, manganous oxide is a powerful base, which readily dissolves in oil; manganic oxide is also readily soluble, yielding fatty acid salts of manganese, and causing oxidation of glycerine. Manganese borate and manganese oxalate are both soluble in oil, the former much more readily than the latter, but they are both salts of little stability at high temperatures in contact with oils. They both dissolve by the aid of heat, forming fatty acid salts of manganese. Borate liberates boric acid under these circumstances, but oxalate yields a mixture of carbon monoxide and carbon dioxide.

Of manganese oleate and linoleate nothing more may be said than that both are extremely soluble in oil, and both easily oxidised from colourless to brown compounds when submitted to the action of air.

The chief adulterants of linseed oil and of boiled oil are cotton-seed oil, rosin oil, and linoleic acid. Cotton-seed, which is to some extent a drying oil, can act as such when mixed with linseed, but when added to olive oil, it behaves as a non-drying oil. In fact, its behaviour is anomalous, and of such a character that it greatly facilitates its extensive use as an adulterating material for the more expensive oils.

Rosin oil is a deleterious adulterant, but one which may be more readily detected than cotton-seed oil. Rosin is

added to boiled oil to hasten its drying; this also is an injurious substance. Of late years glycerine has become an article of greater value than formerly, and this may account for the manufacture of linoleic acid and its use as an adulterant of oleic acid and of linseed oil.

Lastly, it may be mentioned that certain samples of "pale boiled oil" have been found to contain what is practically a raw oil mixed with dryers. Although such oils will dry, their efficiency is nothing like so great as that of an oil "boiled" with a blast of air at a suitable temperature, and, moreover, such oils are deficient in body.

In bleaching vegetable oils, it is necessary to consider the nature of the colouring matters naturally contained in them. These consist of a mixture in varying proportions of the colouring matters known to exist in the leaves of plants, but which, in the case of oils, are derived from the fruit or seeds from which the oils are expressed. There can be no doubt that these substances are closely allied in chemical constitution; they all possess an intensely powerful colouring property, by which is meant that though the colour of some of them may not be dark, yet a very minute weight is capable of imparting a tint to a very large quantity of material.

The names of these substances are:—

Xanthophyll—yellow.

Yellow chlorophyll—yellow.

Blue chlorophyll—blue.

Erythrophyll—red.

In some oils only the xanthophyll and yellow chlorophyll are present; in others, such as olive oil, the yellow and blue chlorophylls occur, and give the liquid a green tint; while in linseed erythrophyll is always present with more or less of the yellow and blue chlorophylls, and some xanthophyll. According to the different proportions of these colouring matters the oil varies in colour. For instance, linseed oil, when brown, contains a mixture of erythrophyll with yellow

and blue chlorophylls ; when greenish brown, the yellow and blue chlorophylls are present in somewhat larger proportion, but mixed with erythrophyll ; while, generally speaking, a bright yellow or pale yellow oil contains xanthophyll only. These substances appear to be combined with the oils, or to be substances of a fatty nature. They are neither dissolved nor acted upon by water, nor by acids diluted with water, when naturally contained in the oils. They are freely soluble in alcohol, and an alcoholic solution is not only susceptible of being destroyed by the joint action of air and water, but by very dilute aqueous solutions of mineral acids, and by acetic acid. In aqueous and alcoholic solutions, light speedily modifies the blue, and eventually destroys all these colours. A solution in turpentine of the isolated colouring matters is also easily destroyed. But, on the other hand, a solution of the colours in melted paraffin wax is comparatively stable.

Zinc hydroxide, copper hydroxide, baryta, potash, and soda easily combine to form metallic salts with blue chlorophyll, less readily, though readily enough with yellow chlorophyll, but far less readily with xanthophyll and erythrophyll. The following facts will serve to show that this is the case. When a solution of the colouring matters contained in green leaves is made by extracting dry, but freshly-gathered, leaves with absolute alcohol, an addition of a saturated solution of baryta water, to the intensely green extract, precipitates first the compound of blue chlorophyll with baryta, then a further addition precipitates the yellow chlorophyll, also as a baryta salt ; but xanthophyll and erythrophyll either remain in solution, or require a much larger addition of the base in order to be precipitated. A crystalline compound of blue chlorophyll with soda is comparatively stable. This substance is, no doubt, formed in green vegetables when they are boiled in water to which some carbonate of soda has been added to maintain their fresh appearance. The addition of a small trace of copper sulphate

to peas and to pickles forms a very permanent copper compound with the colouring matter, which gives an attractive appearance to these articles. Such being an outline of the chief chemical properties of the natural colouring matters contained in oils, the facts mentioned will serve to render the processes for removing the colour from oils more intelligible than they otherwise would be.

Vegetable oils are decolorised, either partially or completely, by the application of one of the following processes :—

1. By the action of light, or by the joint action of light and air.

2. By acids.

3. By saponification.

4. By the action of chlorine.

1. By exposing raw linseed oil to the action of sunlight, it slowly becomes pale in colour, and finally colourless. It is in the highest degree probable that, as oxygen is absorbed by the oil and acid substances are thereby produced, these acids effect the destruction of the colouring matters. In such wise castor oil is bleached.

2. By treating linseed oil with moderately strong sulphuric acid. As the oil and sulphuric acid are of very different specific gravities, it is essential that they be very rapidly and thoroughly mixed by violent agitation. The impurities, such as mucilage and albuminous matters, are thus deprived of water, and more or less charred, and along with them the colouring matters are destroyed by the acid. It is essential for the success of the process that the oil and the acid be not long in contact without undergoing dilution, otherwise the oil itself may become charred. It is, however, possible to obtain oil by this process in a fairly colourless condition, after it has been thoroughly washed with water and allowed to settle.

3. Both rape oil and cotton oil may be rendered of a pale yellow, and even almost colourless, by a process of partial

saponification with caustic alkali of a suitable strength. The colouring matters are saponified, and the resulting soap is of a dark yellow or brown colour, from the colouring matter having combined with the alkali.

4. By the action of chlorine produced in contact with the oil when, for instance, an aqueous solution of bleaching powder is acidified with a cheap mineral acid, such as dilute sulphuric. In this case rapid mixing and violent agitation are essential to the success of the process, otherwise chlorinised products are retained in the oil, which not only confer upon it a distinct flavour and odour, but also cause the oil to solidify with a very moderate lowering of the normal temperature. It is very questionable whether drying oils can with advantage be submitted to such treatment.

5. A variety of methods may be merely mentioned, such as treatment with sulphurous acid, with ferrous sulphate (green vitriol), and potassium dichromate and sulphuric acid.

6. Lastly, the method of Binks, to which reference will be made farther on.

Prof. Hartley next gives an account of certain improvements in the process of oil-boiling, designed with the object of producing a drying oil absolutely free from lead, and, as compared with ordinary oils, absolutely free from colour.

The operations have been carried out, on a manufacturing scale, by Mr. W. E. B. Blenkinsop and himself, and there is no doubt of the practicability of the process.

The process consists in, first, refining the oil, by the removal therefrom of water and mucilage; second, boiling and bleaching the oil at one operation.

It is a fact that water and mucilage can be removed from linseed oil by the action of certain dehydrating substances and solutions of metallic salts, as, for instance, by alum, by strong sulphuric acid, and by a solution of zinc chloride.

There are certain objections to each of these methods, which are of a practical nature: thus, in treating the oil

with strong sulphuric acid, there is too frequently a charring of something, either the oil itself, or of some impurity therein, and this charring, though it may be very slight, has the effect of giving a pale brownish tinge to the oil, which cannot be completely removed by the bleaching process to which the natural colouring matters in the oil are amenable. It is quite true that this brown colour separates sometimes, but it is only after storage for a long period, when a finely divided flocculent matter separates by subsidence. Treatment with zinc chloride is satisfactory but expensive. Perfectly pure manganese sulphate, which is a neutral salt, has been used by Hartley and Blenkinsop in very strong solution, and where there is an objection to using an acid. For ordinary purposes, perfectly satisfactory results are obtained by the use of a dilute sulphuric acid containing about 30 per cent. of  $H_2SO_4$ , since, though it possesses the power of withdrawing water from the oil, it may remain in contact therewith without causing any charring, and at the same time it causes the precipitation in a complete and rapid manner of all the mucilage. A purified linseed oil is thus produced which is bright, clear, and slightly yellowish in colour, though somewhat paler than the ordinary oil. It is important that the strength of the oil should not exceed that degree of concentration which is sufficient for the purpose for which it is intended. The oil having been so treated, and the impurities separated by subsidence or otherwise, it is next submitted to the bleaching and oxidising treatment.

Binks bleached oils with oxides of manganese dissolved in the oil, but difficulty was experienced in carefully regulating the quantity of the manganese compounds which were to be introduced into the oil. For instance, he precipitated manganous hydroxide in contact with oil, and added the mixture to the bulk of the material, and he also modified the treatment by dissolving manganous hydroxide in ammonia, and added the solution to the oil.

Hartley and Blenkinsop prepare manganese linoleate, and

dissolve this in a hydrocarbon, and add a sufficient quantity of the solution to the oil, whereby it dissolves easily and mixes completely. By this treatment, the colouring matter of the oil forms a compound with the manganese which, while it remains in solution, is very speedily oxidised in contact with air, especially when a current of air or oxygen is blown through. The oxidation destroys the colouring matter, and the manganese compound is deoxidised; subsequently it undergoes oxidation again, and the products of such oxidation taking place in the oil are acrolein, formic and acetic acids. After, or concurrently with, the oxidation of the colouring matters, the oil is oxidised, and, at a suitable temperature below 132° F., the oil is bleached, increased in density, and converted into a pale drying oil. By limiting the amount of the manganese linoleate to that which is capable of just oxidising the colouring matters, oils may be bleached with very little further oxidation.

Excellent drying oils have been produced by this process, of a very pale colour. The oil has been used for decorative house painting, for both indoor and outdoor work, on wood and on metal. It has also been used as a coating for iron work, without the addition of a pigment. The plant used in its production is the same as that employed in oil-boiling by the usual processes when a blast of air is used.

The advantages of a pale boiled oil, containing no lead, are the following :—

1. Zinc white retains its pure white colour.
2. Delicate tints, and colours containing sulphides, are not darkened in course of time.

It may be suggested that for indoor decoration, for the painting of ships, railway carriages, railway semaphores, signs, and stations, such oil is free from liability to alter the colours with which it is mixed, owing to its freedom from lead, which is darkened by traces of sulphuretted hydrogen in the air to which such paints are exposed.

Gasometers in gas-works may be painted an unalterable

white with such oil and zinc white. But in this case also the zinc white must be free from lead carbonate or oxide.

In commenting on Prof. Hartley's paper, Mr. Laurie said he had never used linoleate of manganese for boiling with oil, but by the use of borate one did get a boiled oil paler than the oil with which one started. If you take linseed oil which has been already bleached in the sun to a golden yellow, and convert it into boiled oil with manganese, a further bleaching process undoubtedly takes place. An oil prepared with manganese salts, spread on a glass plate, and allowed to dry in the dark, will remain almost colourless, whereas if it were boiled with a lead salt it quickly darkens, even if it is kept away from impure air. Even in a dark room, in pure air, a picture painted with oil boiled with lead will darken. That is another argument in favour of manganese, and he should say it ought always to be used in preparing oil for artistic purposes.

## CHAPTER XIII.

## PAINT MACHINERY.

IN Fig. 40 is shown a complete set of paint grinding and mixing machinery, made by Wright & Co., 157 Southwark Bridge Road, London, S.E., which has given highly satisfactory results in efficiency and economy. It has a set of three granite rollers 30 inches by 15, and two mixing cylinders or pugs, 24 inches in diameter by 25 inches deep, the whole mounted on a strong cast-iron frame. It is made in the following five sizes:—

No.	3-roller Mills. Size of Roller.	Diam. of Pulleys.	Speed of Pulleys.	Weight. (Approx.)	Work turned out per day.	
					Ordinary Colours.	White Lead.
1	in.      in. 16      ×      9	18	70	cwt. 12	tons. $\frac{1}{2}$ to $\frac{3}{4}$	tons. $1\frac{1}{2}$
2	22      ×      12	24	60	16	1 „ 2	4
3	22      ×      14	26	55	22	3 „ 4	8
4	30      ×      15	30	50	30	4 „ 5	10
5	36      ×      16	30	50	35	5 „ 6	12

The utility of having the pug mills placed above the granite rollers is to save labour and space, and the roller mill is kept constantly at work. There are two pugs, one of which is always ready to deliver to the rollers, whilst the other is getting ready by the time the first is being emptied; by this means the output is always going on, and hence great saving both of time and labour. The pugs are

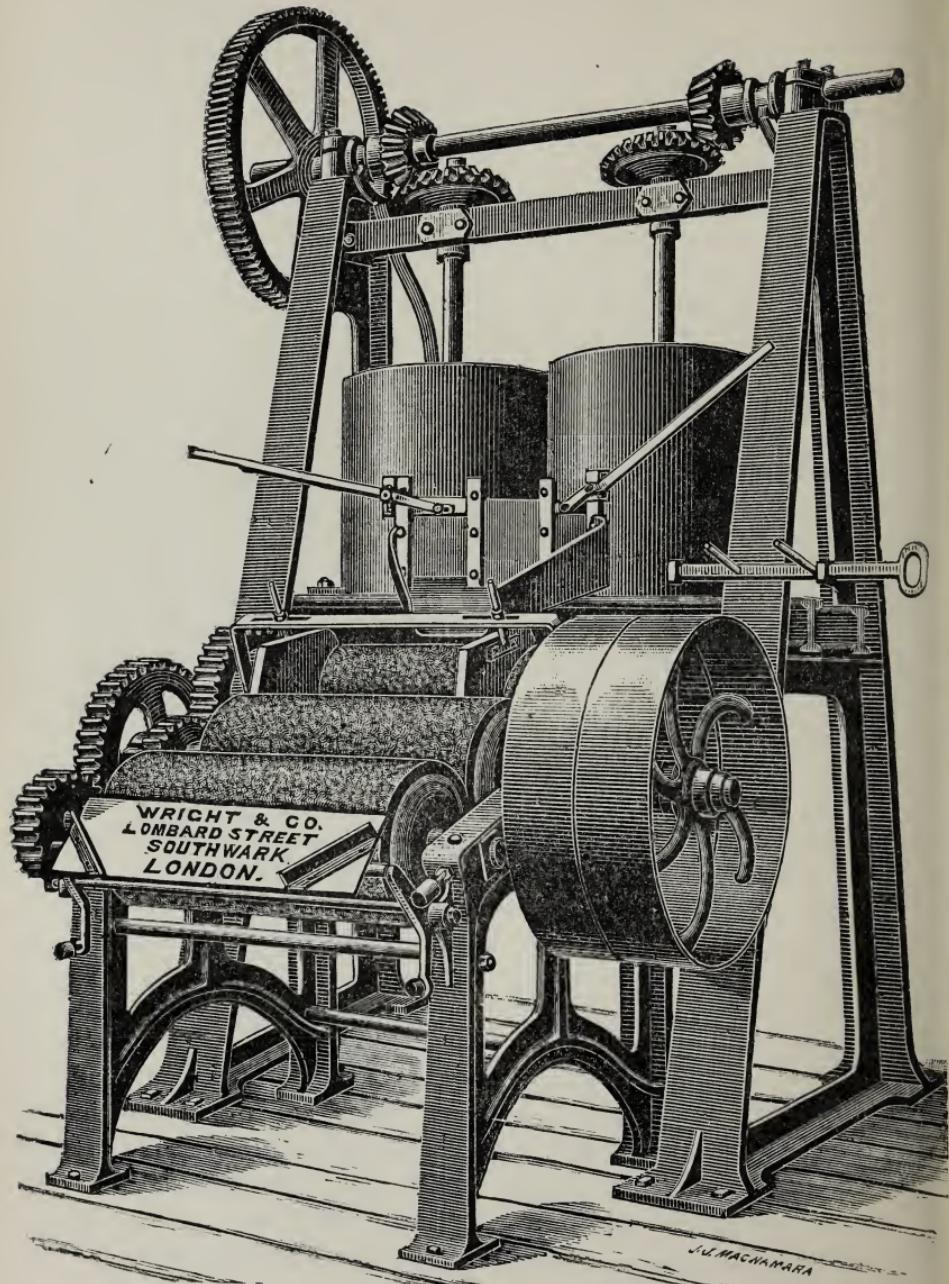


Fig. 40.—WRIGHT'S PAINT MILL.

easily fed from a wooden stage fixed to the frame at the back of pugs. The drawing shows the gear driven by a cog-wheel, but if required it can be driven by fast and loose pulleys. The whole of the machine is very compact.

A handy little grinding machine by the same well-known firm is shown in Fig. 41; a liquid-paint mixer, in Fig. 42; and a single pug mill for paint or putty, in Fig. 43.

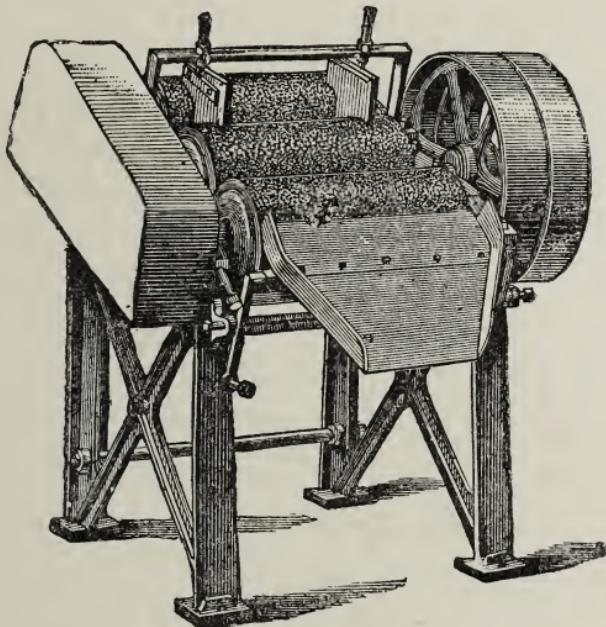


Fig. 41.—WRIGHT'S SMALL PAINT MILL.

Neither of these machines requires any special description, as the mode of application is evident from the illustrations.

This firm are also the manufacturers of Clark's patent paint mill, illustrated in Fig. 44. This mill differs from the ordinary mills in having five instead of three rollers. The material is fed in between the two uppermost rollers, being prevented from spreading too much by means of wooden cheeks shaped so as to fit between the rollers and form a kind of hopper in which the material to be ground is placed. From these two rollers it passes to a third and

fourth placed below, and receives a final grind from the fifth roller in front of the machine, from which it is delivered to the spout as shown. The rollers are all of granite turned

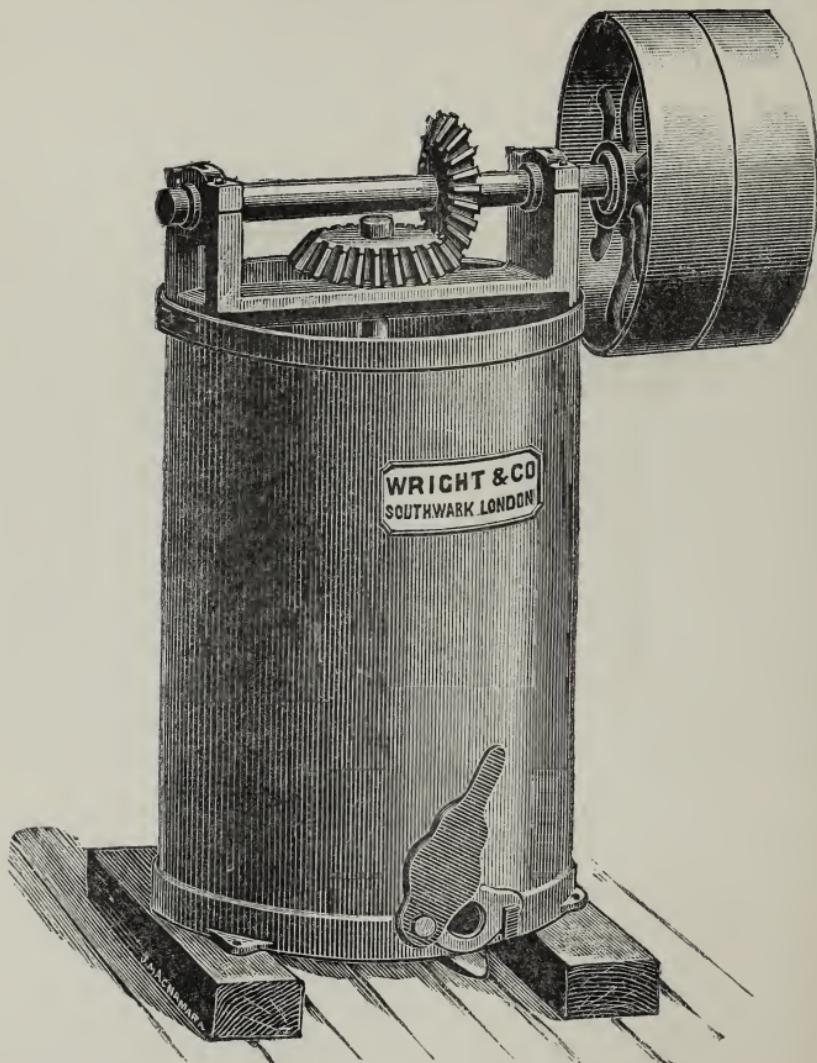


Fig. 42.—LIQUID-PAINT MIXER.

truly cylindrical. They are 15 inches in diameter and are mounted on strong steel spindles. These spindles run on bearings working in guides, by means of which the distance

apart of the rollers and the fineness of the grinding can be adjusted. It will be seen that the driving-shaft of the machine is the lowest of the six shown. It drives by means of spur gearing roller number three, and through it the other rollers of the mill. No two rollers working together revolve at the same speed, and hence one rubs over the other, and they thoroughly grind the material

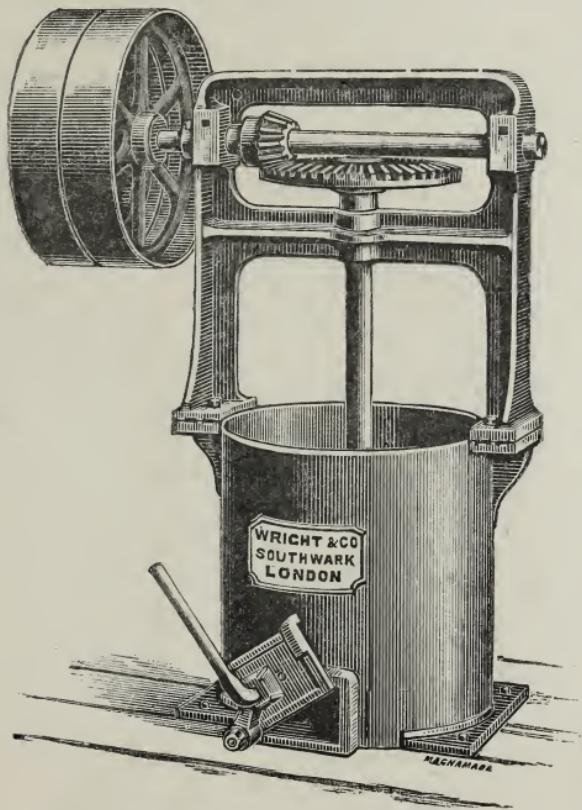


Fig. 43.—SINGLE PUG MILL.

between them. In the common three-roller mills it is necessary to pass the material to be ground through the mill twice, but in this machine one passage is sufficient, so that both time and floor space are saved, as the machine, it is claimed, does the work of two ordinary mills. Another noteworthy feature of this mill is that on No. 2 roller is a

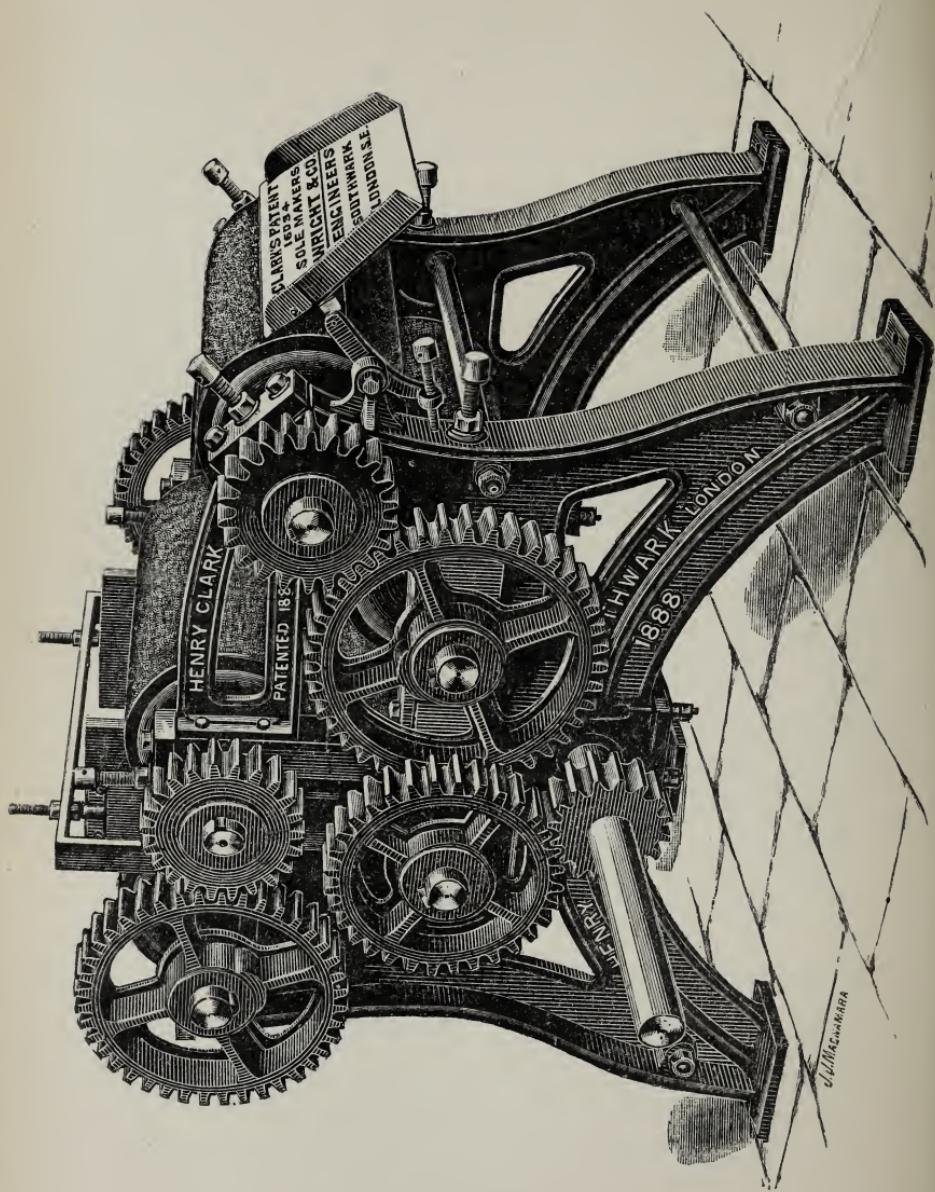


Fig. 14.—CLARK'S PATENT GRAVITY-ROLLER MILL.

lateral motion giving a sidewise movement of  $\frac{3}{4}$  inch. This is also applied to No. 4 roller, and gives the same movement. Each roller can be separately and easily adjusted by means of adjusting screws. The fifth roller is the delivery roller. The weight of No. 2 roller is carried by a strong spring fixed between the bearings of rollers Nos. 2 and 3, so that by the movement of the adjusting screw, the No. 2 roller can be brought down upon No. 3 with the required pressure.

The principle of mounting the rollers of most machines, is that the centre roll shall revolve in fixed bearings, and the two outer ones shall revolve in bearings made to slide backward and forward in grooves in the framework. There is no means of adjusting the rollers in order to keep them in perfect parallel plane, or to compensate for the wear of the brasses. The consequence is, that immediately the bearings begin to wear, the rolls are not then in parallel plane with each other, and the longer they work the worse they get; until they only grind a small distance in the centre of the roll, causing the machine not only to perform imperfect work, but the rolls to wear hollow in the centre.

Hind and Lund, Limited, of the Atlas Works, Preston, Lancashire, claim that in their machine (Fig. 45) these defects are entirely obviated. The centre roll is mounted in a similar manner to other machines, but the two outer rolls are hung upon excentric studs at each side. Should the journals wear at all unevenly, this is at once detached, and by a single turn of the excentric stud at either one side or the other as the case may be, the rolls are kept always in perfect parallel plane.

This machine is fitted with relieving apparatus for throwing the two outer rolls apart whilst working, in case of accident, or for cleaning purposes. Thus the machine may be run for an indefinite period without the granite touching, hence no wear can take place; while the rollers may be instantly put back to their working distances, just exactly as they were before the rolls were thrown apart.

As will be readily understood, this is a very valuable improvement, as the machine can be put in and out of actual grinding work as often as may be desired, without once altering the pressure upon the springs or the grinding distances.

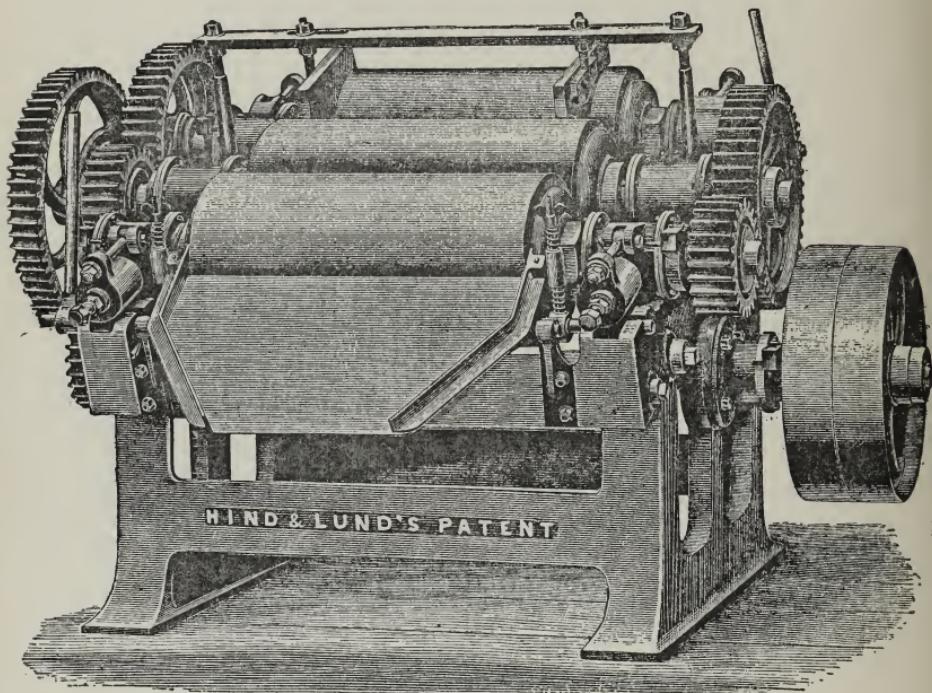
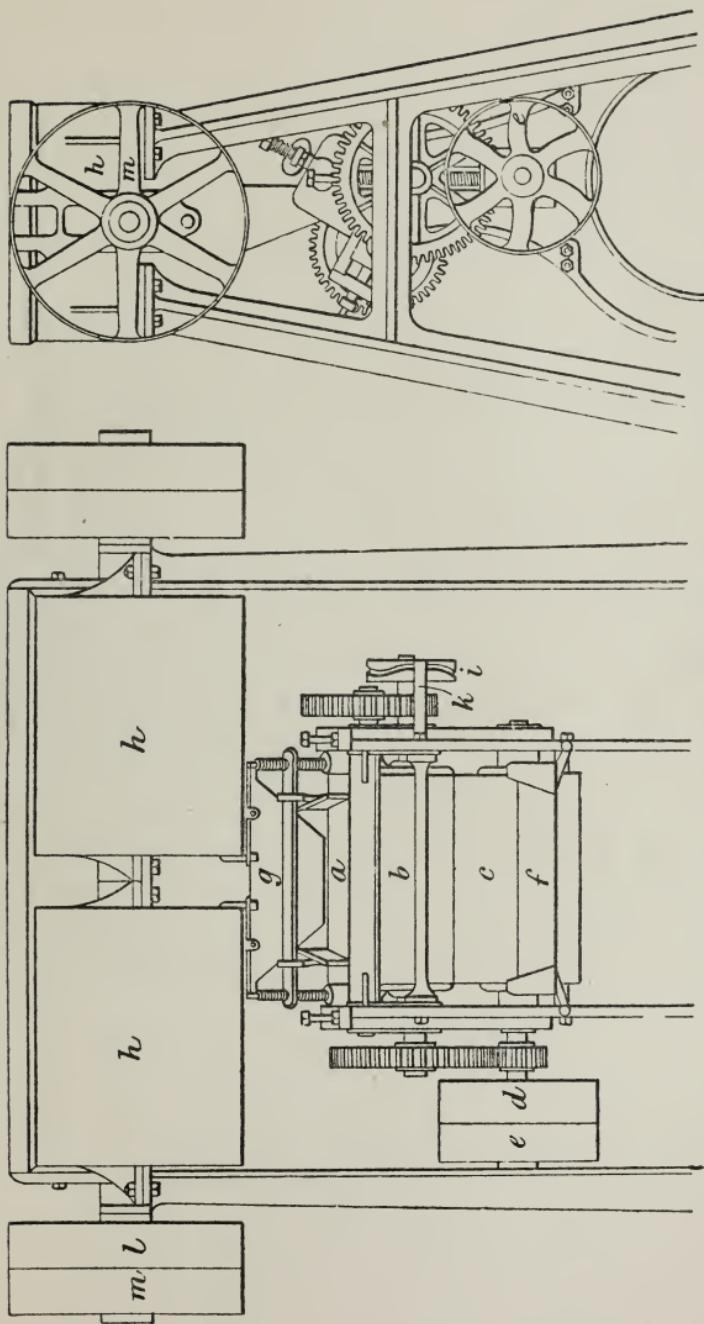


Fig. 45.—HIND AND LUND'S PATENT PAINT MILL.

The bearings are all self-lubricating, and the most delicate colours or white lead can be ground without fear of being deteriorated. The machine too is almost noiseless. Many of them can be seen at work, and giving great satisfaction.

Brinjes and Goodwin's machine is shown in Figs. 46, 47, and 48. The oil and pigments, having been measured or weighed, are placed in the trough *h*. This is provided with



Figs. 46 and 47.—BRINJES AND GOODWIN'S PAINT MILL.

stirrers, similar to those in a pug-mill, which are driven by means of the pulley *l*, *m* being a loose pulley; by shifting the strap on to this, the machine can be stopped at once. When the oil has been thoroughly incorporated with the pigment, the mixture is allowed to run through the spout *g* on the roller *a*. Working against *a* is a second roller *b*, and this in its turn bears upon a third roller *c*. In order to

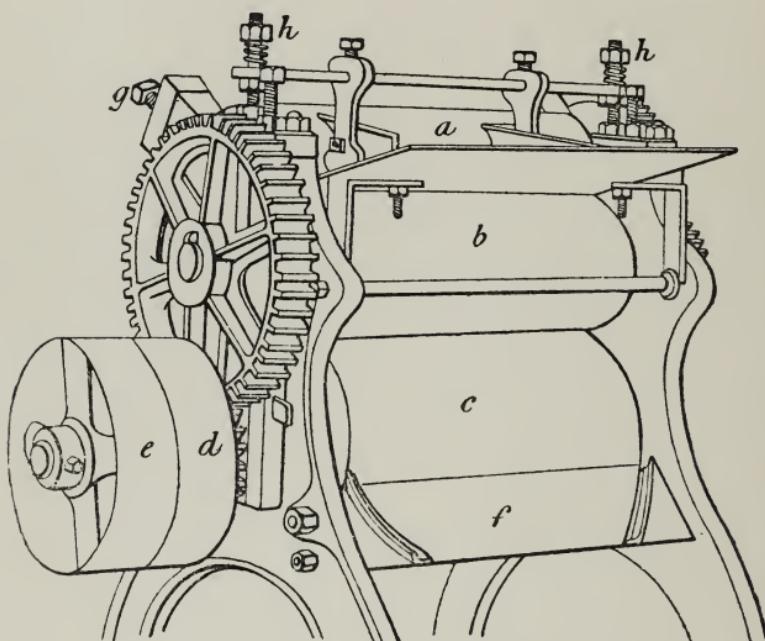


Fig. 48.—BRINJES AND GOODWIN'S PAINT MILL.

prevent the grooving of the faces of the rollers, which always takes place when they revolve in the same plane, there is an arrangement by which a slight lateral motion is communicated to *b*, in addition to the rotary motion. A pin fixed upon the rigid bracket *k* works in the grooved cam *i*, which is keyed on the shaft of the roller *b*. The grinding power of the machine is considerably increased by this modification. The rollers are worked from the pulley *d*;

the loose pulley *e* receives the strap when a pause in the working of the machine becomes necessary. The details of the construction of the grinding machine are given in Fig. 48. The rollers *a b c* are constructed of granite or porcelain; for fine grinding, the latter substance is preferable. They are adjusted by means of the screws *g h*. These are furnished with spiral springs, so that should a nail or other hard substance get between the rollers, these can rise in their bearings, letting the nail fall down at the back. The "doctor" or scraper *f* removes the paint from the surface of the roller *c*; *a b* are also provided with smaller scrapers, which remove any paint that may cake upon their surfaces. Where extreme fineness is requisite, the paint is again passed through the machine, and this operation is sometimes repeated several times.

In working these or any other form of grinding rollers, great care must be taken to clean them thoroughly immediately after use. If the paint be allowed to dry upon the surface of the rollers it is difficult of removal, and interferes with the perfect action of the machine. Should the working parts become clogged with solidified oil, a strong solution of caustic soda or potash will remove it. By means of the same solutions, porcelain rollers may be kept quite white, even if used for mixing coloured paints. Although the colour of most pigments is improved by grinding them finely in oil, yet there are some which suffer in intensity where their size of grain is reduced. Chrome red, for instance, owes its deep colour to the crystals of which it is composed, and when these are reduced to extremely fine fragments, the colour is considerably modified.

PACKING.—When paint is not intended for immediate use, it is packed in metallic kegs. The construction of these, as made by B. Noakes & Co., is shown in Fig. 49. For exportation to hot climates, the rim of the lid is sometimes soldered down, a practice which effectually prevents access of atmospheric oxygen. White-lead paint is frequently

packed in wooden kegs; these prevent the discoloration sometimes caused by the metal of iron kegs. When paint is mixed ready for use, it will, if exposed to the air, become covered with a skin, which soon attains sufficient thickness to exclude the atmospheric oxygen, and prevent any further solidification of the oil. The paint may be still better protected by pouring water over it, or it may be placed in airtight cans. If it has been allowed to stand for some time, it must be well stirred before using, as the pigments have a tendency not only to separate from the oil, but also to settle down according to their specific gravity.

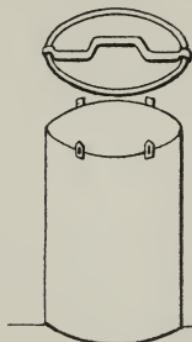


Fig. 49.—PAINT KEG.

## CHAPTER XIV.

## PAINTING.

THE successful application of paint, whether for artistic or preservative purposes, necessitates careful attention to a number of considerations, some of a mechanical and others of a chemical character.

*The Surface.*—Of whatever the surface may be to which the paint is to be applied, great care must be taken that it is perfectly dry. Wood especially, even when apparently dry, may on a damp day contain as much as 20 per cent. of moisture. A film of paint applied to the surface of wood in this condition prevents the moisture from escaping, and it remains enclosed until a warm sun or artificial heat converts it into vapour, which raises the paint and causes blisters. Moisture enclosed between two coats of paint has the same effect. Paint rarely blisters when applied to wood from which old paint has been burnt off; this is probably due to the drying of the wood during the operation of burning.

When the surface to be painted is already covered with old paint, this should be either removed or rubbed down smooth before applying the new. When the thickness of the old coat is not great, rubbing down, accompanied by a careful scraping of blisters and defective parts, will suffice. When the thickness of the old paint necessitates its removal, it may either be burned off, or softened by a solution of caustic alkali, and afterwards scraped. The burning process is the most effective, and leaves the wood in a fit condition to receive the fresh coat of paint; but it is not applicable in the case of fine mouldings. When caustic potash or soda is used, the

paint is left in contact with it for some time, when the linoleic acid of the oxidised linseed-oil becomes saponified, and can easily be scraped or scrubbed off the surface of the wood.

Whenever an alkali is employed, it is of the greatest importance that the wood should afterwards be thoroughly washed several times with clean water, in order to remove every trace of the solvents. Any soda or potash remaining in the pores of the wood would not only retain moisture and cause blistering, but would also have an injurious action upon the vehicle of the paint subsequently applied, and in many cases upon the pigment itself. The remarks already made as to the necessity of an absolutely dry surface should be borne in mind in this instance. When the surface of the paint is to be protected by a coat of varnish, the latter should not be applied until the whole of the oil contained in the paint has solidified. The wrinkling of varnish upon paint is frequently erroneously attributed to the bad quality of the varnish, when the real cause is the incomplete oxidation of the paint itself.

*Priming.*—The first coat of paint applied to any surface is termed the “priming-coat.” It usually consists of red lead and boiled and raw linseed-oil. Experience has shown that such a priming not only dries quickly itself, but also accelerates the drying of the next coat. The latter action must be attributed to the oxygen contained in the red lead, only a small portion of which is absorbed by the oil with which it is mixed.

Kall, of Heidelberg, prepares a substitute for boiled oil by mixing 10 parts whipped blood, just as it is furnished from the slaughter-houses, with 1 part of air-slaked lime sifted into it through a fine sieve. The two are well mixed and left standing for 24 hours. The dirty portion that collects on top is taken off, and the solid portion is broken loose from the lime at the bottom; the latter is stirred up with water, left to settle, and the water is poured off after the lime has

settled. The clear liquid is well mixed up with the solid substance before mentioned. This mass is left standing for 10 or 12 days, after which a solution of potash permanganate is added, which decolorises it and prevents putrefaction. Finally the mixture is stirred up, diluted with more water to give it the consistence of very thin size, filtered, a few drops of oil of lavender are added, and the preparation is preserved in closed vessels. It is said to keep a long time without change. A single coat of this liquid will suffice to prepare wood or paper, as well as lime or hard plaster walls, for painting with oil colours. This substance is cheaper than linseed oil, and closes the pores of the surface so perfectly that it takes much less paint to cover it than when primed with oil.

*Drying.*—The drying of paint is to a great extent dependent upon the temperature. Below the freezing point of water, paint will remain wet for weeks, even when mixed with a considerable proportion of dryers; while, if exposed to a heat of 120° F. the same paint will become solid in a few hours. The drying of paint being a process of oxidation, and not evaporation, it is essential that a good supply of fresh air should be provided. When a film of fresh paint is placed with air in a closed vessel, it does not absorb the whole of the oxygen present; but after a time the drying process is arrested, and the remaining oxygen appears to have become inert.

Considerable quantities of volatile vapours are given off during the drying of paint; these are due to the decomposition of the oil. When the paint has been thinned down by turpentine, the whole of this liquid evaporates on exposure to the air. There must, therefore, be a plentiful access of air, to remove the vapours formed, and afford a fresh supply of active oxygen. The presence of moisture in the air is rather beneficial than injurious at this stage. Especially in the case of paints mixed with varnish, moist air appears to counteract the tendency to crack or shrink. Under the erroneous im-

pression that the drying of paint is a species of evaporation, open fires are sometimes kept up in freshly-painted rooms. It is only when the temperature is very low that any benefit can result from this practice; as a rule, it rather retards than hastens the solidification of the oil, which cannot take place rapidly in an atmosphere laden with carbonic acid.

The first coat of paint should be thoroughly dry before the second is applied. Acrylic acid is formed during the oxidation of linseed-oil, and unless this be allowed to evaporate, it may subsequently liberate carbonic acid from the white lead present in most paints, and give rise to blisters. Sometimes a second priming-coat is given; but usually the second coat applied contains the pigment. This, as soon as dry, is again covered by another coat, and subsequently by two or more finishing coats, according to the nature of the work.

*Filling.*—Before the first coat is applied to wood, all holes should be filled up. The filling usually employed is ordinary putty; this, however, sometimes consists of whiting ground up with oil foots of a non-drying character, and when the films of paint are dry, the oil from the putty exudes to the surface, causing a stain. The best filling for ordinary purposes is whiting ground to a paste with boiled linseed-oil. For finer work, and for filling cracks, red lead mixed with the same vehicle may be employed. For porous hard woods, use boiled oil and corn starch stirred into a very thick paste; add a little japan, and reduce with turpentine. Add no colour for light ash; for dark ash and chestnut, use a little raw sienna; for walnut, burnt umber and a slight amount of Venetian red; for bay wood, burnt sienna. In no case use more colour than is required to overcome the white appearance of the starch, unless you wish to stain the wood. This filler is worked with brush and rags in the usual manner. Let it dry 48 hours, or until it is in condition to rub down with No. 0 sand-paper without much gumming up; and if an extra fine finish is desired, fill again with the same materials, using less oil, but more japan and turpentine. The second

coat will not shrink, being supported by the first. When the second coat is hard, the wood is ready for finishing up by following the usual methods. This formula is not intended for rosewood.

*Coats.*—There is no advantage in laying on the paint too thickly. A thick film takes longer to dry thoroughly than two thin films of the same aggregate thickness. Paint is thinned down or diluted with linseed-oil or turpentine. The latter liquid, when used in excess, causes the paint to dry with a dull surface, and has an injurious effect upon its stability. Sometimes the last coat of paint is mixed with varnish, in order to give it greater brilliancy. In this case, special care must be taken that the previous coats have thoroughly solidified, or cracks in the final coat may subsequently appear. The same remark applies when the surface of the paint is varnished. The turpentine with which the varnish is mixed has a powerful action upon the oil contained in the paint, if the latter is not thoroughly oxidised. The exterior of the paint is thus softened, and the varnish is enabled to shrink and crack, especially in warm weather.

*Brushes.*—The bristles are frequently fastened by glue or size, which is not perceptibly acted upon by oil, and if brought into contact with this liquid alone, there would be no complaints of loose hairs coming out and spoiling the work. It is a common practice to leave the brushes in a paint-pot, in which the paint is covered with water to keep it from drying. The brushes are certainly kept soft and pliant in this way; but at the same time the glue is softened, and the bristles come out as soon as the brush is used. After use, brushes should be cleaned, and placed in linseed-oil until again required, when they will be found in good condition. Treated in this way, they will wear so much better that the little additional trouble entailed is amply repaid. When brushes will not again be required for some time, the oil remaining in them should be washed out by means of turpentine, after which they may be dried without deterioration.

On no account should oil be allowed to dry in a brush, as it is most difficult to remove after oxidation has taken place. The best means are steeping in benzoline for a few days, or in turpentine, with occasional washing in soda-water and with soft-soap, avoiding too violent rubbing.

*Water-colours.*—The manufacture of water-colour paints is more simple than that of oil paints, the pigments being first ground extremely fine and then mixed with a solution of gum or glue. The paste produced in this manner is allowed to dry, after having been stamped into the form of cakes. As soon as the hardened mass is rubbed down with water, the gum softens and dissolves, and if the proportion of water be not too great, the pigment will remain suspended in the solution of gum, and can be applied in the same manner as oil-paint. To facilitate the mixing with water, glycerine is sometimes added to the cake of paint, which then remains moist and soft.

*Removing Odour.*—(1) Place a vessel of lighted charcoal in the room, and throw on it 2 or 3 handfuls of juniper berries ; shut the windows, the chimney, and the door close ; 24 hours afterwards the room may be opened, when it will be found that the sickly, unwholesome smell will be entirely gone. (2) Plunge a handful of hay into a pail of water, and let it stand in the room newly painted.

*Discoloration.*—Light-coloured paints, especially those having white lead as a basis, rapidly discolour under different circumstances. Thus white paint discolours when excluded from the light ; stone colours lose their tone when exposed to sulphuretted hydrogen, even when that is only present in very small quantity in the air ; greens fade or darken, and vermillion loses its brilliancy rapidly in a smoky atmosphere like that of London.

Ludersdorf thinks that the destructive change is principally due to a property in linseed-oil which cannot be destroyed. The utility of drying oils for mixing pigments depends entirely on the fact that they are converted by the

absorption of oxygen into a kind of resin, which retains the colouring pigment in its semblance ; but during this oxidation of the oil—the drying of the paint—a process is set up which, especially in the absence of light and air, soon gives the whitest paint a yellow tinge. Ludersdorf therefore proposes to employ an already formed but colourless resin as the binding material of the paint, and he selects two resins as being specially suitable—one, sandarach, soluble in alcohol ; the other, dammar, soluble in turpentine. The sandarach must be carefully picked over, and 7 oz. is added to 2 oz. Venice turpentine and 24 oz. alcohol of sp. gr. 0·833. The mixture is put in a suitable vessel over a slow fire or spirit-lamp, and heated, stirring diligently, until it is almost boiling. If the mixture be kept at this temperature, with frequent stirring for an hour, the resin will be dissolved, and the varnish is ready for use as soon as cool. The Venice turpentine is necessary to prevent too rapid drying, and more dilute alcohol cannot be employed, because sandarach does not dissolve easily in weaker alcohol, and, furthermore, the alcohol, by evaporation, would soon become so weak that the resin would be precipitated as a powder.

When this is to be mixed with white lead, the latter must first be finely ground in water, and dried again. It is then rubbed with a little turpentine on a slab, no more turpentine being taken than is absolutely necessary to enable it to be worked with the muller ; 1 lb. of the white lead is then mixed with exactly  $\frac{1}{2}$  lb. of varnish, and stirred up for use. It must be applied rapidly, because it dries so quickly. If when dry the colour is wanting in lustre, it indicates the use of too much varnish. In such cases, the article painted should be rubbed, when perfectly dry, with a woollen cloth to give it a gloss. The dammar varnish is made by heating 8 oz. dammar in 16 oz. turpentine oil at  $165^{\circ}$  to  $190^{\circ}$  F., stirring diligently, and keeping it at this temperature until all is dissolved, which requires about an hour. The varnish

is then decanted from any impurities, and preserved for use. The second coat of the pure varnish, to which half its weight of oil of turpentine has been added, may be applied. It is still better to apply a coat of sandarach varnish made with alcohol, because dammar varnish alone does not possess the hardness of sandarach, and when the article covered with it is handled much, does not last so long.

*Composition.*—The composition of paints should be governed—

(1) By the nature of the material to be painted: thus the paints respectively best adapted for wood and iron differ considerably.

(2) By the kind of surface to be covered: a porous surface requires more oil than one that is impervious.

(3) By the nature and appearance of the work to be done: delicate tints require colourless oil, a flattened surface must be painted without oil (which gives gloss to a shining surface), paint for surfaces intended to be varnished must contain a minimum of oil.

(4) By the climate and the degree of exposure to which the work will be subjected: for outside work, boiled oil is used, because it weathers better than raw oil; turps is avoided as much as possible, because it evaporates and does not last; if, however, the work is to be exposed to the sun, turps is necessary, to prevent the paint from blistering.

(5) The skill of the painter affects the composition: a good workman can lay on even coats with a smaller quantity of oil and turps than one who is unskilful; extra turps, especially, are often added to save labour.

(6) The quality of the materials makes an important difference in the proportions used: thus more oil and turps will combine with pure than with impure white lead; thick oil must be used in greater quantity than thin when paint is purchased ready ground in oil, a soft paste will require less turps and oil for thinning than a thick.

(7) The different coats of paint vary in their composition: the first coat laid on to new work requires a good deal of oil

to soak into the material; on old work, the first coat requires turpentine to make it adhere; the intermediate coats contain a proportion of turpentine to make them work smoothly; and to the final coats the colouring materials are added, the remainder of the ingredients being varied according as the surface is to be glossy or flat.

The exact proportions of ingredients best to be used in mixing paints vary according to their quality, the nature of the work required, the climate, and other considerations. The composition of paint for different coats also varies considerably. The proportions given in the following table must only be taken as an approximate guide when the materials are of good quality:—

TABLE showing the COMPOSITION of the different COATS of WHITE PAINT, and the QUANTITIES required to cover 100 yd. of NEWLY-WORKED PINE.

	Red lead.	White lead.	Raw Linseed-oil.	Boiled Linseed-oil.	Turpentine.	Dryers.	REMARKS.
<i>Inside work, 4 coats not flattened.</i>							
Priming .. ..	lb. $\frac{1}{2}$	lb. 16	pt. 6	pt. —	pt. —	lb. $\frac{1}{4}$	Sometimes more red lead is used and less dryer.
2nd coat .. ..	*	15	$3\frac{1}{2}$	—	$1\frac{1}{2}$	$\frac{1}{4}$	* Sometimes just enough red lead is used to give a flesh-coloured tint.
3rd coat .. ..	—	13	$2\frac{1}{2}$	—	$1\frac{1}{2}$	$\frac{1}{4}$	
4th coat .. ..	—	13	$2\frac{1}{2}$	—	$1\frac{1}{2}$	$\frac{1}{4}$	
<i>Inside work, 4 coats &amp; flattening.</i>							
Priming .. ..	$1\frac{1}{2}$	16	6	—	$\frac{1}{2}$	1-8	
2nd coat .. ..	—	12	4	—	$1\frac{1}{2}$	1-10	
3rd coat .. ..	—	12	4	—	0	1-10	
4th coat .. ..	—	12	4	—	0	1-10	
Flattening .. ..	—	9	0	—	$3\frac{1}{2}$	1-10	
<i>Outside work, 4 coats not flattened.</i>							
Priming .. ..	2	$18\frac{1}{2}$	2	2	—	1-8	
2nd coat .. ..	—	15	2	2	$\frac{1}{2}$	1-10	
3rd coat .. ..	—	15	2	2	$\frac{1}{2}$	1-10	
4th coat .. ..	—	15	3	$2\frac{1}{2}$	0	1-10	
							When the finished colour is not to be pure white, it is better to have nearly all the oil boiled oil. All boiled oil does not work well. For pure white a larger proportion of raw oil is necessary, because boiled oil is too dark.

*Area Covered.*—For every 100 sq. yd., besides the material enumerated in the foregoing,  $2\frac{1}{2}$  lb. white lead and 5 lb. putty will be required for stopping. The area which a given quantity of paint will cover depends upon the nature of the surface to which it is applied, the proportion of the ingredients, and the state of the weather. When the work is required to dry quickly, more turpentine is added to all the coats. In repainting old work, two coats are generally required, the old paint being considered as priming. Sometimes another coat may be deemed necessary. For outside old work exposed to the sun, both coats should contain 1 pint turpentine and 4 pints boiled oil, the remaining ingredients being as stated in the foregoing table. The extra turpentine is used to prevent blistering. In cold weather, more turpentine should be used to make the paint flow freely.

According to another authority, it is found that in painting wood, one coat takes 20 lb. lead and 4 gal. oil per 100 sq. yd.; the second coat, 40 lb. lead and 4 gal. oil; and the third the same as the second; say 100 lb. lead and 16 gal. oil per sq. yd. for the three coats. The number of square yards covered by one gallon of priming colour is found to be 50; of white zinc, 50; of white lead paint, 44; of lead colour, 50; of black paint, 50; of stone colour, 44; of yellow paint, 44; of blue colour, 45; of green paint, 45.

*Measuring.*—Surface painting is measured by the superficial yard, girting every part of the work covered, always making allowance for the deep cuttings in mouldings, carved work, railings, or other work that is difficult to get at. Where work is very high, and scaffolding or ladders have to be employed, allowances must be made. The following rules are generally adopted in America in the measurement of work:—Surfaces under 6 in. in width or girt are called 6 in.; from 6 to 12 in., 12 in.; over 12 in., measured superficial. Openings are deducted, but all jambs, reveals, or casings are measured girt. Sashes are measured solid if

more than two lights. Doors, shutters and panelling are measured by the girt, running the tape in all quirks, angles or corners. Sash doors measure solid. Glazing, in both windows and doors, is always extra. The tape should be run close in over the battens, on batten doors, and if the stuff is beaded, add 1 in. in width for each bead. Venetian blinds are measured double. Dentels, brackets, medallions, ornamented iron work, balusters, lattice work, palings, or turned work, should all be measured double. Changing colours on base boards, panels, cornices, or other work, one-fourth extra measurement should be allowed for each tint. Add 5 per cent. to regular price for knotting, puttying, cleaning, and sand-papering. For work done above the ground floor, charge as follows :—Add 5 per cent. for each story of 12 ft. or less, if interior work ; if exterior work, add 1 per cent. for each foot of height above the first 12 ft.

CARRIAGE AND CAR PAINTING.—The following is the substance of an address delivered by McKeon, secretary and treasurer of the Master Car-Painters' Association of the United States :—A first-class railway coach costs, when complete, about 1200*l.* To protect this work, the painter expends 60*l.* to 120*l.* The latter figure will make a first class job. The car has been completed in the wood-shop, and is turned over to the painter, who is responsible for the finish. He is expected to smooth over all rough places or defects in the wood, which requires both patience and skill to make the work look well. Twelve weeks should be the time allowed to paint a car, and it cannot be done in any less time, to make a good job that will be a credit to the painter and all other parties interested in the construction and finish of the car. Too much painting is done in a hurry: proper time is not given the work to dry or become thoroughly hardened before it is run out of the shop, and consequently it does not always give the satisfaction it should ; nor can it be expected that hurried work will be so lasting or durable as that which has the necessary time given to finish it.

*Priming Paint.*—The priming coat of paint on a car is of as much importance as any succeeding one, and perhaps more. Good work is ruined in the priming by little or no attention being given by the painter to the mixing and application of the first coat. The foundation is the support, and on that rests success or failure. The priming should be made of the proper material, mixed with care from good lead and good oil, and not picked up from old paints which have been standing mixed, and must necessarily be fat and gummy, for such are unfit for use on a good job, and will have a decided tendency to spoil the whole work. Special care should be exercised, both in mixing and applying the priming, and it should be put on very light, so that it may penetrate well into the wood. Too much oil is worse than not enough. Good ground lead is by far the best material for the under-coats on a car. Two coats should be given to the car before it is puttied, as it is best to fill well with paint the nail-holes and plugs, as well as defects in the wood, so that moisture may not secure a lodgment, which otherwise will cause the putty to swell, although sometimes unseasoned lumber will swell the putty; and as it shrinks, the nail remains stationary, and of course the putty must give way.

*Best Putty.*—In mixing putty, which may be a small matter with some, take care to so prepare it that it will dry perfectly hard in 18 hours. Use ground lead and japan, stiffening up with dry lead, and whatever colouring you may require in it to match your priming coats.

The next coats, after the work is well puttied, should be made to dry flat and hard. Two coats should be applied, and, for all ordinary jobs or cheap work, sand-papering is all that is necessary for each coat; but when a good surface is required, I would recommend one coat to be put on heavy enough to fill the grain; and before being set, scrape with a steel scraper. The plain surface is all that requires coating and scraping with the heavy mixture. For this coat, which is called filling, use one-half ground lead and any good

mineral which experience has shown can be relied on. This scraping of the panel work will fill the wood equal to two coats of rough stuff, and saves a great amount of labour over the old process, when so much rubbing with lump pumice was done. Sand-paper when the filling is thoroughly hard, and apply another coat of paint of ordinary thickness, when, after another sand-papering, you have a good surface for your colour.

Rough-coating on cars has gone almost out of use, and few shops are now using it to any extent. My experience is that paint has less tendency to crack where rough stuff is left off. I do not claim that the filling was the principal cause of the cracking, if it was properly mixed; but I believe the water used in rubbing down a car with the lump pumice injures the paint, as it will penetrate in some places, particularly around the moulding plugs.

*Finishing Colour.*—The car being ready for the finishing colour, this should be mixed with the same proportion of dryer as the previous coat, or just sufficient to have it dry in about the same time. A great error with many car painters is using a large portion of oil in the under coats, and then but little, if any, in the finishing coats; this has a decided tendency to crack, the under coats being more elastic. Always aim to have colour dry in about the same time, after you have done your priming; by this plan you secure what all painters should labour to accomplish—namely, little liability to crack. Work will of course crack sometimes after being out a few months, or when it has repeated coatings of varnish; and using a quick rubbing varnish on work will cause it to give way in fine checks quicker than anything else. Many of the varnishes used are the cause of the paint cracking, and no painter has been wholly exempt from this trouble.

*Cause of Cracking.*—The most common cause of cracking is poor japan, which is the worst enemy that the car-painter has to contend with. The greater part of the japan is too

elastic, and will dry with a tack, and the japan gold size has generally the same fault, although the English gold size is generally of good quality ; but its high price is an objection to its use. A little more care in the manufacture of japans would give a better dryer, and few would object to the additional cost. Japan frequently curdles in the paint; it will not mix with it, but gathers in small gummy particles on the top. Work painted with such material cannot do otherwise than crack and scale, and the remedy lies only in getting a good pure article of turpentine japan.

In regard to using ground lead, car-painters differ, as some prefer to grind their own in the shop. I use the manufactured lead, and my reasons for doing so are that it is generally finer than any shop can grind it with present facilities, and it has age after grinding, which improves its quality. You can also get a purer lead and one with more body than you can by grinding in the shop, which is a fact that I think most painters must admit. I have tested it very fully, and am convinced on this point.

*Mixing the Paints.*—Permit me to make a few suggestions here in regard to the mixing of paint, which may not fully agree with others' views. There is just as much paint that cracks by putting it on too flat as by using too much oil. Some painters mix their finishing colour so that it is impossible to get over a panel of ordinary size before it is set under the brush, and consequently the colour will rough up. Colour should be mixed up so that it will not flat down for some time after leaving it, and then you have got some substance that will not absorb the varnish as fast as it is applied to the surface. This quick drying of colour is not always caused by want of oil in it, but because there is too much japan, and a less quantity of the latter will do better work, and make a smoother finish. Give your colour 48 hours to dry between coats ; always give that time, unless it is a hurried job, and experience has fully demonstrated that it is poor economy to hurry work out of the shop before it is properly finished.

*Oils, Dryers, and Colours.*—In car-painting, both raw and boiled oils are used, and good work may be done with either, but I recommend oil that is but slightly boiled, in preference to either the raw or the boiled. After it is boiled, if it is done in the shop, let it stand 24 hours to settle, then strain off carefully; this takes out all the impurities and fatty matter from the oil, and it will dry much better, nor will it have that tack after drying that you find with common boiled oil. Use the proper quantity of dryer in mixing your paint, and a good reliable job will be the result. In car-painting, never use prepared colours which are ground in oil, as nine-tenths of such colours are ground in very inferior oil, and they may have been put up for a great length of time, in which case they become fatty, and will invariably crack. These canned colours do not improve with age, as lead and varnish do.

Finishing colours should all be ground in the shop, unless special arrangements can be made with manufacturers to prepare them; and the colour should be fresh, not over 6 or 8 days old after being mixed, and open to the air. Enough may be prepared at a time to complete the coating on a job; but when colour stands over a week it is not fit to use on first-class work, as it becomes lifeless, and has lost that free working which we find in freshly-mixed colours. Such colour may, however, be used upon a cheap class of work, or on trucks, steps, &c., so that nothing need be wasted in the shop.

*Varnishing.*—Three coats of varnish over the colour are necessary on a first-class coach. The first coat should be a hard drying varnish put on the flat colour; the quick rubbing that some use I would not recommend, but one that will dry in five days (in good drying weather) sufficiently hard to rub, is the best for durability. After striping and ornamenting the car, and when thoroughly washed, give a coat of medium dry varnish. Let this stand 8 days; then rub lightly with curled hair or fine pumice, and apply the

finishing coat, which is "wearing body;" this will dry hard in about 10 days, after which the car may be run out of the shop. It should then be washed with cold water and a soft brush, and is ready for the road. In varnishing, many will apply the varnish as heavy as they can possibly make it lie, when, as a consequence, it flows over and runs or sags down in ridges, and of course does not harden properly; this also leaves a substance for the weather to act on. It is better to get just enough on at a coat to make a good even coating which will flow out smooth, and this will dry hard, and will certainly wear better than the coat that is piled on heavily.

Varnishing, we claim, can be over-done, despite some painters' opinions to the contrary. We have heard of those who put  $2\frac{1}{2}$  gal. on the body of a 50-foot car at one application, and we have also listened to the declaration, made by a member of the craft, that he put 2 gal. on the body of a locomotive tank. Such things are perhaps possible, and may have been done; but if so, we know that the work never stood as well as it would if done with one-half the quantity to a coat. In varnishing a car, care should be taken to have the surface clean; water never injures paint where it is used for washing; and a proper attention to cleanliness in this respect, and in the care of brushes used for varnishing, will ensure a good-looking job.

Perhaps your shop facilities for doing work are none of the best, but do the best you can with what you have. Select if possible, a still, dry day for varnishing, especially for the finishing coat. Keep your shop at an even temperature; avoid cold draughts on the car from doors and windows; wet the floor only just sufficient to lay the dust, for if too wet, the dampness arising will have a tendency to destroy the lustre of your varnish. Of course we cannot always do varnishing to our perfect satisfaction, especially where there are 25 or 30 men at work in an open shop, and 6 or 8 cars are being painted, when more or less dirt and dust are sure to get on the work.

A suggestion might here be made to railroad managers, which is that no paint-shop is complete where the entire process of painting and finishing a car is to be done in one open shop. A paint-shop should be made to shut off in sections by sliding doors, one part of the shop being used exclusively for striping and varnishing. I know from experience that nine-tenths of the railroad paint-shops are deficient in this particular, and still we are expected to turn out a clean job, no matter what difficulties we are compelled to labour under.

*Importance of Washing Cars.*—In regard to the care of a car after it has left the shop, more attention should be given to this than is done on many roads. The car should not be allowed to run until it is past remedy, and the dirt and smoke become imbedded in the varnish, actually forming a part of the coating, so that when you undertake to clean the car you must use soda or soap strong enough to cut the varnish before you succeed in removing the dirt. Cars should be washed well with a brush and water at the end of every trip. This only will obviate the difficulty, and these repeated washings will harden the varnish as well as increase its lustre. We know that, in washing a car, where soap is required to remove the dirt and smoke, it is almost impossible to get the smoke washed off clean ; and if it is not quite impossible, the hot sun and rain will act on the varnish and very soon destroy it.

*Re-varnishing.*—Cars should be taken in and re-varnished at least once in 12 months ; and if done once in 8 months it is better for them, and they will require only one coat ; but where they run a year, they will generally need two coats. Those varnished during the hot months will not stand as well as if done at any other time. Painting done in extremely cold weather, or in a cold shop, is more liable to crack than if done in warm weather.

*How to Dry Paint.*—Paint dried in the shop where there is a draught of dry air passing through, will stand better

than that dried by artifical heat; and you will find, by giving it your attention, that work which has failed to stand, and which cracked or scaled, was invariably painted in the winter season, or in cool, wet weather. I have paid some attention to this matter, and know the result.

WOODWORK PAINTING.—One of the attendant drawbacks of houses that are newly built, or have been hastily finished for letting, is the inferior painting of the woodwork, and its speedy destruction. The wood is not thoroughly dry, and the consequence is the preparatory coat does not adhere; the pores being full of dampness, it is impossible for the oil to sink into them, especially as oil and water are unmiscible. Another equally injurious condition is the gum-resin which exudes from the knots of new pine and other timber. Painted over before it has time to come to the surface, the coat is destroyed by the action of the gum. Now, these evils have to be endured so long as the wood has no time to get seasoned. The painter follows the carpenter without any interval of time, and before the action of the weather can bring out the moisture and resinous substances. A coating of shellac is usually given to the knots, though this is often so thin as to be worthless. Crude petroleum, as a perservative coat, is found to be an admirable preparation for the painting. The petroleum is thin, and penetrates the wood, filling up the pores, and giving a good ground for the coats of paint.

According to one American authority, the preparation is of great value. The priming coat should be thin and well rubbed in, and it is better to use a darker colour than white lead as a base. White lead forms a dense covering to the surface, though it has its disadvantages. When petroleum has formed the first coat, two other coats will suffice, one being the priming coat, and a third coat may be given after the work has stood for a season. It is a very desirable plan to leave the painting, or rather finishing coats, for a time, so that any imperfections in the wood or work may be dis-

covered ; it also allows time for any change of colour that may be made. After the priming coat, it is usual in good work to stop all cracks, nail-holes, and other defects with putty ; but in the commoner class of paintings, the coats are laid on quickly, the preceding coat has hardly time to dry before the next is put on, and all the defects of wood, bad seasoning, exudation of gum, &c., quickly begin to show themselves through and disfigure the work.

A good paint ought to possess body, power of covering, and flow evenly from the brush, and become hard. Though zinc white has less body than white lead, it is more durable, and will stand sulphur acids without blackening. Some colours stand better than others ; the ochres, Indian and Venetian reds, burnt and raw umber, are reliable, and may be used without scruple. It is also worthy of notice that salt air acts injuriously on white lead, and zinc white is therefore preferable in situations exposed to the sea-air. (*English Mechanic.*)

IRON PAINTING.—The decay of iron becomes very marked in certain situations, and weakens the metal in direct proportion to the depth to which it has penetrated ; and although where the metal is in quantity this is not very appreciable, it really becomes so when the metal is under  $\frac{3}{4}$  inch in thickness. The natural surface of cast iron is very much harder than the interior, occasioned no doubt by its becoming chilled, or by its containing a large quantity of silica, and this affords an excellent protection.

But should this surface be at all broken, rust immediately attacks the metal and soon destroys it. It is very desirable that the casting be protected, and a priming coat of oil or paint should be applied for this purpose ; the other coats, though requisite, can be given at leisure.

The following is a process to which all cast-iron water pipes should be submitted. It was introduced by Dr. Smith, and is equally applicable to any other casting that can be manipulated :—Each casting is thoroughly dressed, and made clean

and free from the earth and sand which cling to the iron in the moulds, hard brushes being used in finishing the process to remove the loose dust. Every casting must be likewise free from rust when the paint is applied. If the casting cannot promptly be dipped after being cleansed, the surface must be oiled with linseed oil to preserve it until it is ready to be dipped. No casting is on any account to be dipped after rust has set in. The coal-tar pitch used as a paint in this process is made from coal-tar distilled until the naphtha is entirely removed and the material is deodorised. In England it is distilled until the pitch is about the consistence of wax. The mixture of 5 or 6 per cent. of linseed oil is recommended by Dr. Smith. Pitch which becomes hard and brittle when cold will not answer for this use. Pitch of the proper quality having been obtained, it must be carefully heated in a suitable vessel to a temperature of 300° F., and must be maintained at not less than this temperature during the time of dipping. The material will thicken, and deteriorate after a number of pieces have been dipped; fresh pitch must, therefore, frequently be added, and occasionally the vessel must be entirely emptied of its old contents and refilled with fresh pitch. The refuse will be hard and brittle like common pitch, and consequently worthless for the purpose. Every casting must attain a temperature of 300° F., either by previous heating or during the immersion before being removed from the vessel of hot pitch. It may then be slowly removed, and laid upon skids to drip. In the case of water pipes, all those of 20 inches diameter and upwards will have to remain at least 30 minutes in the hot fluid to attain this temperature. The coating when cold should be tough and tenacious, and not brittle nor have the slightest tendency to scale off.

In considering the painting of wrought iron it must be noticed that when iron is oxidised by heating in contact with the atmosphere, two or three distinct layers of scale form on the surface, and, unlike the skin upon cast iron, can be readily detached, as by bending or by hammering the metal.

The outer layer of this scale is more highly oxidised than the inner, and is slightly redder in tinge from the presence of a variable excess of ferric oxide over that contained in the inner layer. The oxide occurring in the outer scale is fusible only at a high temperature, is strongly magnetic, and slightly metallic in lustre ; while the inner layers are more porous, dull, and non-metallic in lustre, less brittle, and also less powerfully magnetic. It will be seen that the iron has a tendency to rust from the moment it leaves the hammer or rolls, and that the scale above described must come away. One of the plans to preserve the iron has been to coat it with paint when still hot at the mill ; and although this answers for a while, it is a very troublesome method, which iron-masters cannot be persuaded to adopt, and the subsequent cutting processes to which it is submitted leave many parts of the iron bare. Besides, a good deal of the scale remains, and until this has fallen off, or has been removed, any painting over it will be of little value. The only effectual way of preparing wrought iron is to effect a thorough and chemical cleansing of the surface of the metal upon which the paint is to be applied, that is, it must be immersed for three or four hours in water containing from 1 to 2 per cent. of sulphuric acid. The metal is afterwards rinsed in cold water, and, if necessary, scoured with sand, put again into the acid bath or pickle, and then well rinsed.

The real value of any paint depends upon the quality of the linseed oil, the quality and character of the pigment, and the care bestowed on the grinding and mixing, and as all this is entirely a matter of expense, cheap paints are not to be relied upon. The superiority of most esteemed paints is due to the above causes rather than to any unknown process or material employed in the manufacture.

The following excellent article on the preservation of iron and steel structural work appeared in the ‘Illustrated Carpenter and Builder.’ It conveys the most recent American opinion.

One of the most important economic questions of the

present day is the preservation of iron and steel structures. In America many millions of dollars are annually spent in the erection and construction of these, and the amount is increasing in rapid proportion. Bridges, buildings, viaducts, ships, and machinery are now being made of these materials, to almost the entire exclusion of others. From their very nature iron and steel are peculiarly subject to decay from atmospheric and other influences. The question of preserving them is not merely one of finance, but, especially in the case of railroads, one affecting the lives and property of a large portion of the community. What, then, is the best method of preserving them?

The almost universal method is by means of paints, or the application of substances to their surfaces which will resist or retard the influence of air, water, and other destructive agencies. The requisites of a good paint for this purpose are that it shall adhere firmly to the surface, and not chip or peel off, thereby leaving portions of the surface exposed. It must not corrode the iron, else the remedy may only aggravate the disease. It must form a surface hard enough to resist influences which would remove it by friction, yet elastic enough to conform to the expansion and contraction of the metal by heat and cold. It must be impervious to and unaffected, as far as possible, by moisture, atmospheric and other influences to which the structure may be exposed.

The paints that have been used for this purpose are principally asphalt and coal-tar paints, consisting of mineral and artificial asphalt or coal-tar, either applied alone or combined with each other, and, more or less, with metallic bases, and iron oxide paints and lead oxide paints, especially red lead, in all of which the pigment is held to the surface of the iron or steel by combination with linseed oil. The choice of paints must lie, so far as our present practical experience goes, between these three classes, zinc oxide being found to be entirely unsuitable on account of a pro-

pensity to peel off. What, then, is found to be the experience in actual practice with these? Asphalt and coal-tar paints "run" when exposed to the sun and other sources of heat, which is a serious matter with vertical surfaces; and after a time become extremely brittle and scale off entirely, leaving the under surface exposed, unless the paint is constantly renewed. In the meantime the exposed iron and steel are being corroded by rust. Iron oxide paints, including "metallic brown," are paints made from iron ore, or by some chemical process with an iron base. These are invariably iron in a greater or less degree of oxidation, or in other words, rusted iron. Now it is well known that one of the most active promoters of rust or decay in iron is the rust itself. Under the combined influences of the moisture and carbonic acid of the atmosphere, iron oxide or iron rust becomes a carrier of oxygen from the air to the metal, rust begetting rust. It is therefore evident that this material alone has no preserving effect on iron; in fact, it promotes its decay.

How is it when combined with linseed oil in the form of paint? In the economy of nature, iron oxide is a great disinfectant. When in contact with organic matter and moisture, even at a low temperature, under favourable conditions, it readily gives up oxygen, destroying more or less the organic matter, and being itself reduced to a lower oxide. When thus reduced, with equal readiness it absorbs oxygen from the atmosphere, and again passes it on, thereby promoting and eventually ensuring the destruction or transformation of the organic matter with which it may be in contact, either in the soil or elsewhere. The same process appears to take place when combined with linseed oil in the form of paint and exposed to atmospheric influences, the oil being the organic matter. If linseed oil in drying formed an air- and water-proof film, it might be urged that the oxide of iron would be entirely protected from the direct influences of oxygen of the air and moisture. Such however is not the case.

The most eminent authorities have recently shown that the dried film of linseed oil, unless united with a pigment that combines chemically and forms a water-proof coating with it, actually absorbs water very much like a sponge. Where water will go air will also go, and we thus have in direct contact with the iron oxide of the paint, which does not combine chemically with oil, those elements, air, moisture, and organic matter, which cause the iron to become a carrier of oxygen and a destroyer of what it is in contact with. It is well known that iron paint darkens with age; this is caused largely by the iron oxide losing oxygen, which is partly transferred to the oil, burning it up and destroying its tenacity, as may be seen by examining iron structures painted for some time with iron paint or metallic brown, the paint being found extremely brittle and in feathery scales. This is not all the damage that is done. The iron oxide in the paint becomes a carrier of oxygen to the very metal it was designed to protect, and the process of corrosion is commenced and carried on under the paint, which eventually peels or scales off, the surface of the metal being found more or less oxidised and corroded.

Asphalt and iron oxide being thus shown to be entirely incapable of preserving the iron, it remains for us to consider the effect of red lead. This pigment has the property of forming with linseed oil a hard elastic coating, clinging with great tenacity to the metal. It has no oxidising effect on iron, and does not act as a carrier of oxygen from the atmosphere after the paint has set, neither does it render the oil brittle nor promote rust. When red lead fails, it is principally by gradual wear or friction from the outside. It does not scale or blister, which both asphalt and iron oxide paints will do, thereby requiring a thorough scraping and removal of old material before a new coat can be applied. Any red lead pigment adhering to the metal forms a permanent base for subsequent paintings, and is utilised in further preserving the metal. The U.S. Government

specifications for ironwork in the new Library Building of Congress provide that "all the work not Bower-Barffed must be given one coat of pure red lead paint--not metallic paint of any kind, but pure red lead--before leaving the shop and becoming rusted."

The experiments of the U.S. Navy Department on the preservation and fouling of plates covered with different pigments may be interesting. A plate of iron covered with asphalt paint was immersed in sea-water for eight months and six days at the U.S. Navy Yard, Portsmouth, N.H. At the end of that period it was found to be covered with scum and mud, and very badly rusted. A plate coated with iron paint, immersed at Key West, Fla., was found to be covered with branch shell and coral, but little paint remaining, and very badly pitted and rusted. A plate with two coats of red lead, at the Norfolk Navy Yard, was found to have a few barnacles attached, but to be in fair condition, with no rust whatever on the iron after the paint was removed. It will be seen that not only did the red lead protect the iron better than the other pigments referred to, but that the plates were in far better condition as regards barnacles and fouling. The superiority of red lead being thus established, it is adopted for use on hulls of U.S. Government warships.

On the Dutch State railroads a series of experiments extending over a period of three years were made with the above pigments on scrubbed plates, as well as those which had been pickled in acid to remove the scale. It was found that the red lead was superior in each case to the others.

If red lead is thus proved to be the best pigment for preserving iron and steel structures, what is the proper method for applying it? We have seen above that the value of red lead depends upon its forming certain combinations with the oil, and actually setting very much the same as plaster of Paris or cement sets when mixed with water. To successfully work with the latter substances, it

is necessary to put them in shape as quickly as possible after mixing with water before the setting takes place. If the chemical action of setting has partly taken place, the material may be moulded, but it is known that good results will not be obtained. Red lead, like these substances, must be applied to the work before it sets with the oil. It is on this point that failures in the use of pigment have generally occurred, because if it be applied after the combining or setting process has taken place, the hard, elastic, clinging coating will not be formed on the iron surface.

The following is the practice of one of the largest ship-building establishments in applying red lead to the hulls of vessels. The plates are first pickled in a dilute solution of muriatic acid ; then passed between rapidly revolving wire brushes, which remove all scale and dirt, leaving the iron with a bright, smooth surface ; then thoroughly washed with pure water, and rubbed entirely dry ; and immediately coated with red lead and pure raw linseed oil. The red lead is first thoroughly mixed with just enough linseed oil to form a very thick, tough paste, which will keep for several days without hardening. This paste, as wanted for use, is thinned down to the proper consistency for spreading with pure linseed oil, and applied at once, care being taken to leave paint-pots empty at night. A gallon of paint thus prepared contains about 5 lb. of oil and 18 lb. of red lead, and will cover on first coat about 500 square feet. In this way the red lead and oil get their initial set on the surface of the iron, and the closer the pigment is brought to the iron the more durable will it be found. Some parties prime iron with iron oxide paint or metallic brown before applying red lead, which appears to be a mistake, as this paint readily scales from iron, and, of course, carries the lead with it. Others coat the iron with oil before applying the red lead. This, too, prevents the adhering paint from coming in contact directly with the surface, and should be avoided, provided the iron is properly prepared by thorough cleaning and

removal of any scale and moisture, which is a matter of the greatest importance.

In priming wood surfaces which are absorbent of oil, the best practice favours the putting on of a coat of pure oil, or oil thinned with turpentine, which shall penetrate the surface, and form a binder for the subsequent coats. With iron, the case is quite different, provided we have a paint which, from its very nature, can attach itself firmly to the surface, because it is out of the question for it to hold on to the surface of iron by any process of absorption into the pores of the metal, as linseed oil will not penetrate to any extent. Such a paint should be put directly on the surface of the clean, dry metal, as is done in the cases of Government vessels referred to, without the intervention of a coat of oil or other substances.

The rusting of iron before the application of paint, which is sometimes recommended, should by all means be avoided, as it not only prevents the contact of the paint with the metal, but induces a chemical action which may go on with its corroding work under the applied paint.

As to the relative cost of iron oxide paints and red lead, there is no doubt that the first cost of painting structures with iron oxide is somewhat less than with red lead. The best railroad authorities state, however, that labour in painting structural work costs twice as much as material. The true economy must therefore be sought in the durability of the paint as well as the preservation of the structure from rust. Actual experiments have shown that structures painted with iron paint had to be repainted in the third or fourth year, those with red lead not until the sixth year.

In the second painting with iron paint, the old material must be entirely removed before a fresh coat can be properly applied, entailing considerable increased cost, whereas with the red lead no such expense is necessary, but, as before stated, a portion of the pigment remains on the iron, continuing to protect the surface, and is the very best base for

the new coat, besides contributing materially towards it, lessening the expense of each repainting. It will therefore be easily seen that, although in first cost red lead may be slightly dearer than the iron paint, yet in the long run it will be greatly cheaper, besides giving assurance, for the reasons above stated, that the structure is not deteriorating from the effects of the atmosphere and paint.

Before closing, it might be well to allude to the effect of lampblack when mixed in small quantities, say an ounce to the pound of red lead. It changes the colour to a deep chocolate, a possible advantage in some cases, and also prevents the red lead from taking its initial set with linseed oil as quickly as when mixed with oil alone. Experiments recently made showed that this compound would remain mixed in paste form with linseed oil some thirty days without hardening. Thorough mixture is of the greatest importance, and should be done in the dry state before adding the oil. If rapid drying is desired, Japan dryer can be mixed with the oil used in thinning the paste before application with the brush.

Too much stress cannot be laid on the great importance of having the metallic surface perfectly clean and as free as possible from scale and rust before the application of the paint. Where pickling with acid is impracticable, as is frequently the case in railroad and other structural work, thorough brushing with wire brushes should be resorted to.

FRESCO PAINTING.—The following observations are due to Prof. Barff, who dealt with the subject in one of the Cantor Lectures given at the Society of Arts.

The ground upon which fresco is painted is a lime ground; and in order to have a permanent picture, it is clear we must have a firm and stable ground. In order to prepare that ground, first of all the wall must be absolutely dry; there must be no leakage of moisture from behind. Lime which has been "run" (as it is technically called by builders) for a year or a year and a half is best to be employed, for in pro-

portion as the lime has been carbonated (though it must not be so to too great an extent) by the action of the carbonic acid of the air it makes a better and a harder mortar. With this lime must be mixed sand, and a great deal depends on the selection of the sand. It must be river sand, and it should be of even grain; the sand should be mixed with water, and allowed to pass along down a small stream, so that in the centre of the stream you would have sand grains pretty nearly equal in size. This is a point of considerable importance. The reason why new lime cannot and ought not to be used is because it blisters; small blisters appear on the surface, and that of course would be ruinous to a picture. A well-plastered wall should not have a blister or crack in it, and this is secured by having your lime run for some time, of good quality to start with, and mixed with good sand. There is no chemical process that takes place in fresco painting other than this, that silicates are formed by the action of the lime upon the sand, and carbonates by the action of the carbonic acid of the air upon the lime.

In painting a fresco picture, inasmuch as there is no re-touching the work when it is finished, the artist must make his drawing very carefully. The cartoon is made upon ordinary paper, then it is fixed against the wall where the picture is to be painted. The part where the artist decides to begin his work is uncovered, that is to say, a portion of the paper is turned down and cut away, but in such a manner that it may be replaced. Then the plasterer puts fresh plaster, about an eighth of an inch thick, upon the uncovered portion of the wall, and the plasterer's work is of the utmost importance in fresco painting. The workman ought to practise it well before he attempts to prepare the ground for a large picture, and it is of the greatest importance to allow the man to practise for several weeks before he is allowed to prepare any portion of the ground, even for decorative painting. In this way he becomes accustomed to the suction of the wall, and upon the suction of the wall depends

the soundness of the ground and the success of fresco painting.

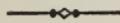
When the plaster is first put on, of course it is very soft ; the piece of cartoon is replaced upon it, and the lines of the picture are gone over with a bone point, so that an indentation is made, and then the artist begins his painting. At first he finds his colours work greasy ; you cannot get the tint to lie on, it works streaky ; but you must not mind that, you must paint on, but you must only paint on for a certain time, for if you go on painting too long you will interfere with the satisfactory suction of the ground, which is so necessary to produce a good fresco painting. Of course, nothing but practice can tell any one the period at which he ought to stop. After some practice, you know perfectly well by the feel when you ought to stop. If you feel your colour flowing from your brush too readily, you ought to stop at this period. You must then leave your work for a time, and go back to it again. And then you will find, as the plaster sucks in the colour which you have first laid on, that there will be—it may be in the course of half-an-hour, it may be an hour, that depends upon the temperature of the atmosphere—a pleasant suction from your brush, the colour going from it agreeably, and you will find that it will cover better. Now is the time to paint rapidly, and complete the work you have in hand. When the colour leaves your brush as though the wall was thirsty for moisture, you should cease painting ; every touch that is applied after that will turn out grey when it dries, and the colour will not be fast upon the wall.

You will see, then, how impossible it is, with such materials, to paint in the same style in which you paint a picture in oil-colour. Fresco painting involves the adoption of an entirely different style from oil painting. The frescoes of the old masters are not highly wrought up, highly-finished works. They depend for their effect upon the juxtaposition of tints, the shadows being intensified by lines and cross-

hatching. If you look at those reproductions of some of the most valuable fresco paintings of the old masters, you will see the method adopted by them depended upon the juxtaposition of tints, not upon covering over, and over, and over again. That juxtaposition of tints produces roundness, transparency, and has a very pleasing effect upon the eye. If two tints are put against one another, they do not appear to us as if they were single, but each adds something to the effect of the other, and together they produce a pleasurable and agreeable effect, if they have been properly selected. We all know how tempting it is to go back to a piece of painting and do something to it that ought to have been done before. We think that a touch will improve it, and we go and make it: but in fresco painting the temptation must be resisted, for it will be absolutely fatal to the permanency of the work.



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